

CHEMICAL ABSTRACTS

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1—APPARATUS

C. G. DERRICK

Some new apparatus for routine analysis. JEAN DURAND and JEAN VERNAY. *Chimie et industrie* 10, 207-11(1923).—Illustrated description of app. at the Lab. of the Acieries de la Marine (France) for making a large no. of *N detns. in metals, volatile matter in coal, and acid and alkali titrations*, also, *hot water wash bottle*, and a *nozzle with automatic check valve* for washing large numbers of ppts. A. PAINNEAU COUTURE

Automatic sampler for liquids in industrial operations. LUDWIG FUCHS. *Z. Zuckerind. czechoslov. Rep.* 47, 435-6(1923).—A branch line diverts part of the main stream of liquid to the device. A collecting vessel has one outlet in the form of a small-bore glass tube, ending near the bottom of the vessel, bent upward to form a siphon, and delivering to a sample container outside. A second siphon of large pipe serves for emptying. The heights of the siphons are so related that as the liquid rises in the collection vessel, the sampling siphon begins to operate when the vessel is about half full, and the emptying siphon when it is nearly full. A reduction in area of the collecting vessel at the level of the top of the emptying siphon causes a rapid rise in level and hence insures positive action of the emptying siphon. W. L. BADGER

A new inductor for conductivity determinations with the use of an alternating current. FERD. SCHEMINZKY. *Biochem. Z.* 136, 336-8(1923). See *C. A.* 17, 2374, 2801. GEORGE ERIC SIMPSON

Sulfur trioxide smoke tubes for determining air currents. S. H. KATZ and J. J. BLOOMFIELD. *Bur. Mines, Repts. of Investigations* 2505, 2 pp.(1923); 1 illus. The app. used to det. flow of air, direction of the currents, and the rate of mixing consists of a glass tube contg. fuming H_2SO_4 on granular pumice stone, attached to a rubber syringe bulb. A squeeze of the bulb blows air through the tube causing the evolution of a stream of dense white smoke. After prepn., the tubes are sealed and when ready for use are broken at a file scratch on both ends and inserted into a rubber nipple at the bulb. W. H. BOYNTON

Electrical carbon monoxide recorder. M. MOELLER. *Siemens Z.* 3, 226-33 (1923).—The basic principle of this recorder is the increase in temp. and elec. resistance of a Pt wire mounted in a tube through which a mixt. of the gas plus O_2 is bypassed. The greater the proportion of CO and H in the gas mixt., the hotter the Pt wire and the higher its elec. resistance. C. G. F.

Lumen meter. JOHANN SAHULKA. *Elektrotechn. Z.* 44, 665-6(1923); cf. *Ibid* 39, 253(1918).—A modification of the previously described integrating photometer. D. MACRAE

Salt resistance thermostat. P. E. DEMMLER. *Chem. Met. Eng.* 29, 368-9(1923).—The principle of operation depends on the rapid change in the elec. resistance of a salt near its m. p. Solder pots, habbit pots, etc., can be controlled within $\pm 3^\circ$ to 5° at 500° . When the tube of salt immersed in the solder nears the m. p., sufficient current passes to trip a relay that operates the switch cutting off the heating current. E. G. R. ARDAGH

Art of sealing base metals through glass. WM. G. HOUSSKEEPER. *J. Am. Inst. Elec. Eng.* 42, 954-60(1923); cf. *C. A.* 15, 212; 17, 691.—Methods are described whereby base metals, in particular Cu, may be sealed to and through glass of a different expansion coeff. A large surface of contact is provided between the glass and metal and the metal so proportioned that the stresses resulting from the differences in coeff. of expansion are less than the ultimate strength of the joint. Four types of seals are discussed: the flattened wire seal for small elec. conductors; the ribbon seal for special purposes; the disk seal for com. manuf. of seals for carrying about 100 amps.; the tube seal in which metal and glass tubing are joined together. D. MACRAE

Glass-to-metal joint. C. H. MEYERS. *J. Am. Chem. Soc.* 45, 2135-6(1923).—

Clean glass with chromic acid, rinse and dry; coat metal part with Sn or solder, clean with ZnCl_2 , wash and dry. Hold the 2 parts together above a flame and when Sn melts insert glass in the metal.

D. F. SHARP

New process for the volumetric estimation of ammonia and carbamide nitrogen by the hypobromite method. J. TILLMANS AND A. KRÜGER. *Z. angew. Chem.* 35, 686-7 (1922).—A simple glass app. is described for the estn. of NH_3 or carbamide by the hypobromite method. It consists essentially of an upper cylindrical portion provided with a ground-glass stopper and a draw-off cock drawn out to a fine opening. The upper vessel fits with a ground-glass joint into a lower vessel and communication between them is established through a vertical tube extending nearly to the top of the upper chamber, which is charged with brine to a level of 3-4 cm. below the top of the vertical communication tube. When the draw-off cock is opened and the app. is otherwise closed, brine runs out until equil. is attained between the inside and outside pressures. The lower vessel being previously charged with hypobromite soln., the reaction is then started by rotating a boat contg. the carbamide or NH_4 salt on its axis so that its contents fall into the soln., and the N evolved causes the displacement of an equal vol. of brine from the upper vessel through the draw-off cock. The boat is fixed to a horizontal axis which is ground to pass through, and fit into a tubulure in the side of the lower vessel, and the boat can be reversed by turning the projecting portion of the axis through 180° . The app. can be utilized for *urine investigations* by placing the urine in the lower vessel, and running in the hypobromite by means of a tap funnel through the vertical communication tube.

J. C. S.

Indirect boiling. K. HELLNER. Swed. 50,779, Jan. 25, 1922. An app. consisting of a rotary boiler provided with outside heating elements which rotate with the boiler. The heating bodies are fitted with steam pipes. An efficient heating is attained by the thorough circulation of the boiling liquid over the heating surfaces.

Condensing apparatus for vapors or moist gases. A. E. W. HOBCHENSTROEM. Swed. 54,019, Mar. 14, 1923.

Extraction apparatus. C. W. A. KLEINE. Swed. 50,741, Jan. 25, 1922.

Emptying bottles. A. M. PALMEN. Swed. 52,807, Oct. 4, 1922. A new *siphon arrangement*.

2—GENERAL AND PHYSICAL CHEMISTRY

GEORGE L. CLARK

The preparation and publication of research papers. A. W. DOX. *Am. J. Pharm.* 95, 356-61 (1923).—An explanation of what research papers are and of how best to prepare them for publication.

W. G. GAESSLER

The geometrical order and the chemical action of atoms. H. J. PRINS. *Chem. Weekblad* 20, 402-3 (1923).—After polemical remarks against Hermanns (*C. A.* 17, 2873) P. states that the chem. activity of an atom is not detd. by its place in the mol. but by its energy content.

R. BRUTNER

Röntgenographic determination of the structure of rolled metal foils. II. H. MARK AND K. WEISSENBERG. *Z. Physik* 16, 314-8 (1923); cf. *C. A.* 17, 2208.—In rolled foils of Ag, Al, Au, Cu and Pt 2 independent groups of space lattices have been found. The first is characterized by the fact that a $[112]$ direction lies parallel to the rolling direction with a scattering of 8° , and a $<110>$ plane parallel to the plane of rolling with a scattering of $\pm 35^\circ$. For the second group a $[100]$ direction lies parallel to the rolling direction with a scattering of 8° , and a $<100>$ plane is parallel to the plane of rolling with a scattering of 40° . For Au and Pt the 2 types are approx. equally intense in X-ray effect, while for Cu and Al the first is much more prominent.

G. L. CLARK

The properties of chemical compounds and the arrangement of electron orbits in their molecules. C. A. KNORR. *Z. anorg. allgem. Chem.* 129, 109-40 (1923).—This important paper embodies the first serious and comprehensive attempt to apply the Bohr conception of the dynamic atom to mols. of all degrees of complexity and to the interpretation of the properties of chem. compds. It is an outgrowth of the researches and ideas of Willstätter, Hantzsch, Fajans, Pummerer and Herzfeld. The chief concern is with homopolar compds. (*e. g.*, org. compds., diamond, mols. of gaseous elements) in which there is "atomic" linkage by the sharing of electrons. Instead of static electrons at cube corners, etc., (Kossel-Lewis-Langmuir) it is assumed that the shared electrons move in an approx. radial direction as in the uncombined atoms and that

the plane of the orbit contains the line joining the kernels, rather than being perpendicular. In an ideal homopolar compd. the orbit actually encloses both kernels of the bound atoms. Fajans (*Naturewissenschaften* 11, 165(1923)) has shown that there is a more or less gradual transition between ionic and at. linkages by deformation of the electron orbits of the anion by the influence of the cation. Some substances may be considered either from the standpoint of deformed ions or of at. linkage. The electron

constitution of methane may be represented by $\text{H} \begin{array}{c} \text{H} \\ \parallel \\ \text{C} \\ \parallel \\ \text{H} \end{array} \text{H}$, in which the lines are

not valences but eccentric orbits of binding electrons enclosing both C and H kernels. The formula shows the C atom with the completed Ne shell of 8 electrons, and H with the He shell. This differs from the Lewis-Langmuir cubic atom not only in postulating motion but also a definite electron shell is inscribed around the H nuclei so that the mol. surface is electronic and possesses properties of symmetry and internally compensated forces like those of rare gas atoms. Several properties may be studied as criteria for at. linkage, viz., slowness of reactions, lack of electrolytic disoc., isomerism, light absorption, and particularly volatility. The more volatile a compd. the more nearly perfect is the at. linkage and the more nearly like a rare gas. The following expression assists in the formulation of the electronic structures: $J = V - [(nS + p2) \cdot A]$, where J is the no. of electrons given up to the outside (or + charge), A is the no. of electrons shared by 2 atoms or at. groups, V is the no. of valence electrons in the neutral atoms, n the no. of octets, and p the no. of doublets. Numerous examples and applica-

tions are given. The formation of ammonium ion is as follows: $\text{H} \begin{array}{c} \text{H} \\ \parallel \\ \text{N} \\ \parallel \\ \text{H} \end{array} + \text{H} \rightarrow$

$\text{H} \begin{array}{c} \text{H} \\ \parallel \\ \text{N}=\text{H} \\ \parallel \\ \text{H} \end{array} \rightarrow$. N in NH_3 has an unshared electron pair in eccentric orbits

which may enclose a H nucleus; the arrow indicates that the extra electron is relegated to the outside and may be easily attached to another atom resulting in an ionic linkage. The NH_4^+ ion with its at. linkages and electron orbits enclosing H has a surface like that of a single atom, accounting for the strong resemblance to the alkali ions. It has always been difficult to show why the diphenyliodonium group $(\text{C}_6\text{H}_5)_2\text{I}^+$ is similar to a monovalent metal. The structure of diphenyliodonium hydroxide is easily shown

as follows: $\left[\begin{array}{c} \text{C}_6\text{H}_5 \\ \parallel \\ \text{C}_6\text{H}_5 \end{array} \text{I} \right]^+ \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{H} \end{array} \right]^-$. The I atom with 7 valence electrons combines by sharing electron pairs in common eccentric orbits with 2 phenyl groups. After formation of the octet configuration, 1 electron is available (arrow) which completes by ionic combination the O octet (6 valence + 1 originally from H and now one of a shared pair + 1 from the ionic combination). Of very great

interest is the case of triphenylmethyl and its compds: (1) $\left[\begin{array}{c} \text{C}_6\text{H}_5 \\ \parallel \\ \text{C}_6\text{H}_5 \end{array} \text{C} \right]$, free radical, unstable and colored because of unsatn. of the C (only 7 electrons); (2)

$\left[\begin{array}{c} \text{C}_6\text{H}_5 \\ \parallel \\ \text{C}_6\text{H}_5 \end{array} \text{C} \right]^- \left[\text{Na} \right]^+$, anion, colored and conducting; (3)

$\left[\begin{array}{c} \text{C}_6\text{H}_5 \\ \parallel \\ \text{C}_6\text{H}_5 \end{array} \text{C}=\text{X} \right]$, pseudo-salt formed by at. linkage, colorless and nonconducting;

(4) $\left[\begin{array}{c} \text{C}_6\text{H}_5 \\ \parallel \\ \text{C}_6\text{H}_5 \end{array} \text{C} \right]^+ \left[\begin{array}{c} \text{X} \\ \parallel \\ \text{X} \end{array} \right]^-$, unsatd. cation (triphenylmethylcarbo-

onium salts), colored and conducting. In benzene it is very likely that 3 electrons

are shared by each C-C combination. On the other hand in alkali polyhalides, only 1 electron in an eccentric quantum orbit may be shared by 2 halogen atoms, or

for KI₃, $\left[\begin{array}{c} \diagup \quad \diagdown \\ | \quad | \\ \text{---} \text{I} \text{---} \text{I} \text{---} \text{I} \text{---} \\ | \quad | \\ \diagdown \quad \diagup \end{array} \right] \leftarrow \left[\text{---} \text{K} \text{---} \right]^+$, a structure well in keeping

with the properties and crystal structure. Other examples are the chloro-oxy acids, higher complex compds. such as phosphomolybdic ions, and atoms with higher coordination nos. In conclusion the 4 possible types of chem. binding and electron orbit dispositions exemplified by various crystal lattices are as follows: atomic,

$\text{--} \text{--} \text{--}$, diamond; ionic, $\oplus \quad \ominus$, CsF; molecular, $\oplus \ominus$, ice;

metallic, $\oplus \text{---} \oplus$, Na.

G. L. CLARK

The electronic theory of valency. II. Intramolecular ionization in organic compounds. T. M. LOWRY. *Trans. Faraday Soc.* (preprint) 1923.—L.'s theory of intramol. ionization (*C. A.* 17, 913) is extended to org. compds. by postulating that double bonds can assume a form in which one C atom carries *eight* L-electrons while the other C atom carries but *six*, only one pair of electrons being shared. The former atom is negatively and the latter positively charged. This type of bond, called a "mixed double bond," is represented as contg. one covalency and one electrovalency. Acetylene is represented as contg. a "mixed triple bond," made up of one electrovalency and two non-polar, or covalent bonds. Most anomalies of org. chemistry are considered due to the development of electrovalencies within the mol. L. states that reactivity in org. chemistry can be ascribed to the same cause as reactivity in inorg. chemistry, namely, to a process of ionization. However, the ions in org. chemistry are usually "bound" instead of "free." The resting states of the mols. are not necessarily identical with their reactive phases. A polar double bond may not necessarily represent the most stable form of an unsatd. compd. The mols. may undergo a preliminary process of activation before reacting chemically. The views put forward make it possible to assign a definite chem. meaning to the process of activation, since in many cases this process may consist simply in the conversion of covalent into electrovalent bonds. It is suggested that org. compds. might be divided into two groups according as the normal structure of the mol. is polar and therefore reactive, or is non-polar and must undergo isomeric change into a polar form before it can react. Some mols. may be permanently polar. The metallic derivs. of org. radicals must have a polar nature like

that assigned to Na⁺Cl⁻. Zinc methyl $\text{Zn}^{++} \begin{array}{l} \text{CH}_3^- \\ \text{CH}_3^- \end{array}$ and the Grignard reagent

$\text{Mg}^{++} \begin{array}{l} \text{CH}_3^- \\ \text{CH}_3^- \end{array}$ should exist only in a polar form. Metals play an important part as

"key-atoms" in maintaining the "induced alternate polarities" of a conjugated mol. Quinquevalent N may also act as a key-atom. Fully satd. compds. are non-polar unless ionizable. An electrovalency can be developed in a system made up entirely of single bonds only by breaking one of the covalencies and so producing two independent ions instead of the bound ions that are formed by the rupture of a double bond. The reactivity of a satd. compd. may depend, therefore, on the readiness with which this conversion of a covalency into an electrovalency can occur. The theory of "mixed double bonds" is also applied to the phenomena of conjugation. From this point of view a conjugated compd. is one which, in its reactive form, contains an unbroken series of positive and negative charges on alternate atoms. The theory is also used in considering compds. which may yield tautomeric ions. In the case of the Na deriv. of Et acetoacetate, the Na atom acts as the key-atom and induces alternating polarities throughout the chain. It is tautomeric since a H ion may attach itself to any one of the negative poles (*C. A.* 17, 2240). **III. The transmission of chemical affinity by single bonds.** *Ibid* (preprint) 1923.—L. suggests that the existence of alternate polarities in satd. systems is still unproven and states that the small fluctuations which are observed in the strength of unsatd. acids as the double bond is moved along the chain may be attributed to steric influences. Certain radicals which increase the strength of an acid are said to be "acylous." The amino group is acylous. However, the acylous character of this group is commonly masked by the formation of internal salts.

L. M. HENDERSON

Some density determinations. A. C. EGERTON AND W. B. LEE. *Proc. Roy. Soc. (London)* **103A**, 487-99 (1923).—A method for the accurate detn. of the d. of small amts. of metals to about 1 part in 10,000 was sought. The Archimedes method was used. The use of a mobile and dense org. liquid avoids air bubble difficulties and damping, and increases the wt. of the liquid displaced. Ethylene bromide was here used. The use of a very fine Al wire, and correction for surface tension effects on the wire, make it possible to apply the method accurately even to small samples (1 g.) of the metal. Incidentally, accurate detns. of the density and h. p. of ethylene bromide and CCl_4 in the range 15–20° were made. The prepn. of a satisfactory sample of metal for d. detn. was accomplished by filtering through a capillary, casting, and heating *in vacuo*, all in glass. The density of Pb was detd. as 11.3437 at 20°, with a probable error of 1 part in 100,000. The d. of a sample of U-Pb, 11.2960 at 16°, corresponds to an at. wt. of 206.26. Detns. of the d. of a 1.5 g. sample of Cd agree to 1 part in 20,000.

R. S. MULLIKEN

Determination of the density of charcoal by displacement of liquids. J. B. FIRTH. *Trans. Faraday Soc.* (advance proof) **1923**. The apparent ds. of coconut shell charcoal and sugar charcoal were detd. after definite intervals of contact with various liquids. The d. increases with the time of contact between the liquid and charcoal. It is concluded that the difference in the observed ds. of charcoal in various liquids is largely detd. by the sorption attraction between the charcoal and the liquid and to a much lesser degree by the capillary forces exerted in the system.

L. T. FAIRHALL

The coefficient of viscosity of helium and the coefficients of slip of helium and oxygen by the constant deflection method. M. N. STATES. *Phys. Rev.* **21**, 662–71 (1923).

Using the const. deflection method S. extends the measurements of Stacy and Van Dyke on the coeffs. of slip in CO_2 and air to the gases He and O_2 . The nature of the surface of the cylinders influences the coeff. of slip, the latter changing from 123 and 61.1 in He and O_2 for a rough surface, to 160 and 64.5 for a polished surface. The classical theory of Maxwell demands that the slip for these gases be 191 and 70, resp. S. ascribes his low values either to the presence of reverse specular reflection, or to the liberation of O_2 from the walls of the cylinder. The coeff. of viscosity for He at 23° is 1.0623×10^{-4} . This is 2% less than the value obtained by the capillary tube method, but is believed to be correct to 0.1%.

L. B. LOEB

Structure association. GUSTAV HELLER. *Z. angew. Chem.* **36**, 351 (1923).

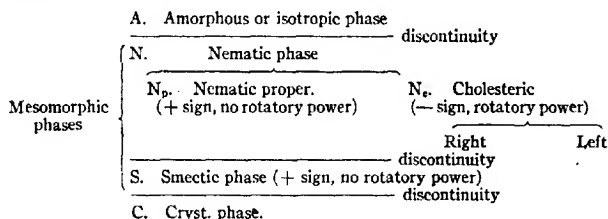
The tendency of certain substances, notably *p*-lactones, isatol, hydroxyindazole and γ -hydroxyquinoline, to maintain a trimol. state in soln. appears to present a new kind of association, *structure association*. Certain solvents are, however, in some cases able to resolve this polymeric form. Thus, while isatol is trimol. in PhOH, hydroxyindazole indicates therein mainly a bimol. form. In boiling AcMe hydroxyquinoline is trimol., shows beginning dissoc. in more dil. camphor melts, and has the simple mol. wt. in PhOH. Therefore such substances may be regarded either as mono- or as trimol.

W. O. F.

The mesomorphic states of matter. G. FRIEDEL. *Ann. phys.* **18**, 273–474 (1922).

This paper is a complete treatise upon the types and properties of matter existent between the true amorphous and cryst. states. The condition formerly designated as liquid crystals or anisotropic liquids is divided into 2 classifications: *smectic* (from *σμηγμα* = soap), and *nematic* (from *νημα* = thread). These correspond, resp., to Lehmann's "fließende Krystalle" and "flüssige Krystalle" or the French classification "liquides à coniques" and "liquides à fils." The former is identified by a waxy consistency and is practically a normal condition for soaps, while the latter is characteristic of elongated org. mols. such as azoxyphenetole, etc. In the nematic state the mols. are distributed at random but have a common direction; a subgroup, the *cholesteric* state, includes nematic substances subjected to torsion and is optically negative. Neither should diffract X-rays. In the smectic state the mols., in addn. to having a common direction, are arranged in equidistant parallel layers. Such substances should reflect X-rays in a manner similar to that by a set of parallel at. planes in solid crystals. (A mixt. of K oleate, glycerol and H_2O has planes 43.5 Å. apart according to de Broglie.) The optical properties of the mesomorphic states, obviously the most important means of exptl. study, are described in great detail together with geometric interpretations. Thus it is shown that a smectic substance contains no other discontinuity of structure than certain focal cones. The focal domains are governed by a family of cycloides of Dupin, i. e., parallel surfaces to which the optical axis is perpendicular. In the nematic state there is nothing similar. Smectic substances have graduated, step-like drops revealing a unique direction of planes with discontinuous properties, and rectilinear flow not characteristic of the nematic. The smectic have peculiar rods (batonnets)

elongated from spherical form, and revealing large variations from const. surface energy depending upon the direction, while nematic have spherical droplets and const. surface energy independent of the direction. These and many other characteristics differentiate the 2 types into the definitive mol. arrangement—in layers or random. Cholesteric substances are characterized by selective reflection of circularly polarized light, a strong rotatory power, and by the appearance of fine lines and network visible in ordinary light and accentuated between nicols—the planes of Grandjean. Over 60 pages are devoted to the proof that the cholesteric form is really a nematic state. Matter is thus classified as follows:



42 compds. are classified according to this scheme, illustrated by 32 beautiful photomicrographs. Of the salts of the *cholesteryl* radical ($C_{27}H_{46}$) with aliphatic acids, the formate to the butyrate ($C_4H_7CO_2$ —) have a single phase, the cholesteric (the *cholesteryl* radical dominating); the caprylate ($C_8H_{17}CO_2$ —) to the myristate ($C_{14}H_{27}CO_2$ —) have 2 phases, cholesteric and smectic; the stearate and oleate have 1 phase, smectic (the acid radical dominating).

G. L. CLARK

A relation between surface tension and density. ALLEN FERGUSON. *Trans. Faraday Soc.* (advance proof) 1923.—F. has derived an expression which defines the const. C in Macleod's empirical surface tension formula for unassociated liquids ($\gamma = C(\rho_l - \rho_g)^{1/2}$), where ρ is the d., in terms of the mol. wt. and crit. consts. of the liquid concerned. The calcd. values for C for various liquids agree very well with the observed values.

L. T. FAIRHALL

The form of a crystal as a function of superficial energy and its density. CONSTANTIN HRYNIAKOWSKI. *Bull. soc. chim.* 33, 548-50 (1923).—A mathematical paper concerned with a system of 2 phases, liquid and crystal. The following expression is derived: $(dK/d\sigma)\sigma + K = F[\sigma M_k - f(M_k/d)]$, where K is the superficial energy per unit surface, σ the sp. surface, M_k the mass of the crystal, F and f functions, and $f(M_k/d)$ is the phase surface.

G. L. CLARK

Properties of powders. VI. Compressibility of powders. E. E. WALKER. *Trans. Faraday Soc.* (advance proof) 1923.—Methods have been devised for measuring the resistance of powders to compression by (a) static loads and (b) blows from a falling weight. The resistance offered by powders made from Pb, NH_4Cl , KCl , NH_4NO_3 , $NaCl$, KNO_3 , $CaCO_3$, $Ba(NO_3)_2$, and trinitrotoluene to both these forms of compression has been investigated. With Pb shot, compression takes place by the deformation of the particles, and since the load-vol. curves of NH_4NO_3 , trinitrotoluene and mixts. of these 2 substances are very closely similar in form to the load-vol. curve of Pb it is supposed that these substances are compressed in very much the same way as Pb. On the other hand, $Ba(NO_3)_2$, NH_4Cl and $CaCO_3$ (pptd.) develop during compression a white opaque appearance devoid of coarse structure, indicating that the original particles have disintegrated. It is suggested that powders made from KCl , KNO_3 and $NaCl$ are compressed chiefly by deformation of the particles when static loads are used but that blows break up the particles which first fall together in closer order, thus making the powder appear more compressible. As compression proceeds the particles are further disintegrated and a hardening effect is manifested, causing the resistance to compression to rise more rapidly. **VII. The distribution of densities in columns of compressed powders.** *Ibid* (advance proof) 1923.—Local ds. in columns of compressed powders have been measured and the form of the d. gradient curve has been detd. From this curve the distribution of pressure in a column of compressed powder has been deduced.

H. JERMAIN CRRIGHTON

Properties of powders. The variation of pressure with depth in columns of powders. J. H. SHAXBY AND J. C. EVANS. *Trans. Faraday Soc.* (advance proof) 1923.—Measurement of the av. vertical pressure p_x at various depths x in columns of Pb shot and of

fine and coarse emery indicates an exponential increase of p with x . The abs. value of p appears to be dependent on the state of packing of the column, and the resulting shape of equal-pressure surfaces. The general form of the pressure depth curves agrees well with the equation $p_a = p_m(1 - Ce^{-kx})$, in which p_m is the max. pressure and C and k are consts.

H. JERMAIN CRRIGHTON

Electrical properties of gels. FELIX MICHAUD. *Compt. rend.* 177, 30-2(1923); cf. *C. A.* 17, 2528. —Gelatin or gelose gels expand at the cathode and contract at the anode when a p. d. is imposed. Expts. show that a gel subjected to a pressure gradient shows a p. d. The part under highest pressure loses its positively charged liquid and the part of least pressure gains positively charged liquid. The relation between the difference of pressure and the p. d. is called the "coefficient of mechanical electricity." It is the one characteristic which det. all the properties of a gel. A difference of 10^4 bars or 0.1 atm. produces a p. d. of about 1 milliv. The opposite sides of a semipermeable membrane adsorb differently because they are under different pressures and consequently have a p. d. between them. This may explain nutrition. A tactile nerve sensation may be an elec. current started by unequal pressures. With strong currents, the excitability of a nerve decreases near the anode because it dries out and increases near the cathode because it becomes hydrated and more permeable. F. E. BROWN

The formula of A. Einstein, $\eta/\eta_0 = 1 + 2.5\phi$ and the viscosity of tannin solutions. A. V. DUMANSKII AND H. K. TARASOV. *J. Russ. Phys. Chem. Soc.* 49, 1, 186-92(1917). —The Einstein formula, $\eta/\eta_0 = 1 + 2.5\phi$ (*Ann. Phys.* [1] 34, 391(1911); cf. *C. A.* 5, 2995) in which η = the internal friction of the solu., η_0 = the internal friction of the solvent and ϕ = vol. occupied by the solute in 1 cc. of solu. is called, for such cases in which the particles of the solute are larger than those of the solvent. Since this latter condition is fulfilled in colloidal sols, an attempt was made to test the applicability of the formula to sols of tannin of various concns. The values for η/η_0 were obtained by detg. with Ostwald's viscosimeter the viscosity of the sols and solvent at various temps., making use of the formula $\eta/\eta_0 = \tau d_0/\tau_0 d$, in which τ_0 = time of outflow of solvent, τ = time of outflow of sol., d_0 = density of solvent and d that of the sol. The densities of the sols were detd. from the formula, $d = d_0 + c \cdot (cd_0/d')$, where c = concn. of solute in g. per 1 cc. of sol and d' = d. of solute. This d. formula was also written as $(d - d_0)/c = (d' - d_0)/d' = \text{const.}$, and $\phi' = c/d'$. Since the above consts. had been previously detd., the values for d of the sols at various concns. and temps. could be calcd. Finally in applying the above data to the Einstein formula the latter was expressed as $\eta/\eta_0 = 1 + 2.5\phi'c$. From the extensive tables given for various concns. (0.0025-0.25 g. per 1 cc.) and at temps. of 20°, 40°, 60° and 80° it is readily observed that: (1) ϕ' is not a const. value; (2) it increases with the concn.; (3) it approaches a const. only when the concn. is small; (4) av. values for ϕ' so obtained are greater than those calcd. on the basis of the d. of tannin; (5) ϕ' becomes more const. at the higher temps. Points (1), (2) and (3) are explained by the statement that the colloidal particle has a greater vol. because it is surrounded by a layer of solvent. This layer is formed in the course of motion of the particle in a viscous medium (hydrodynamic vol.) and secondly because of the force of attraction operating between the colloidal particle and the mols. of the solvent. At high temps., with the attendant increased velocity of motion of the solvent mols., the vol. of these spheres should decrease, which supposition is borne out by the observed values of ϕ' . The existence of such spheres can explain the great increase of the viscosity of sols with increasing concn. and hence the increasing value of ϕ' . For the viscosity of the solvent immediately surrounding the colloidal particle must have a different value from that of the viscosity of the solvent by itself. If the Einstein formula be changed to $\eta/\eta_0(1 + kc^2) = 1 + 2.5\phi'c$, where k is a const., then it is shown that it will hold well for the conditions and observations detailed above. That k is a const. for any given temp. was verified. W. A. P.

The thickness of adsorbed gas layers. J. J. HAAK. *Physica* 2, 12-4(1923). —The thickness of an air layer, adsorbed by a bright Hg surface, is measured by the reflection of light, as observed by a *Babinet compensator* (*Ann. Physik* 39, 488(1890)). The measurement is first made on pure Hg *in vacuo*, and then in the presence of air. The thickness is found to equal about 5 layers of mols., while Langmuir found that only one layer is adsorbed. R. BRUTNER

Adsorption experiments with various charcoals. LUDWIG PINCUSSEN. *Biochem. Z.* 137, 117-20(1923). —The adsorption of methylene blue by charcoals from various sources (Merck, casein, glucose, sucrose) in various sols. (contg. different acids or alkalis, salts with different cations, or different anions) is detd. Results are to be evaluated later. GEORGE ERIC SIMPSON

Negative adsorption. I. The relation between negative adsorption and electrolytic dissociation. M. A. RAKUZIN. *J. Russ. Phys. Chem. Soc.* 53, 1, 369-73 (1921).—Lagergreen (cf. Wo. Ostwald's Grundr. d. Kolloidchem. 1909, p. 406) observed that porous substances, such as kaolin and charcoal, absorb out of solns. not the solute but the solvent, and he named this phenomenon *negative adsorption*. In the present article R. shows that this occurs only when the porous substance, the adsorbent, is in contact with solns. of crystalloids, whether electrolytes or nonelectrolytes, but not when it is in contact with true colloidal solns. of amorphous substances. Thus a piece of kaolin (porous plate) absorbed only H_2O out of aq. solns. of NaCl and sucrose, while it adsorbed irreversibly caramel out of its aq. soln. A partial explanation for the negative adsorption of the solvent from solns. of electrolytes is offered on the basis of the inadsorbability of ionized substances (Freundlich, *C. A.* 1, 1094). With negative adsorption of the solvent from solns. of nonelectrolyte crystalloids (sucrose) a new type of dissoc. is suggested but not discussed. **II. The law for the absorption of solvent in negative adsorption.** M. A. RAKUZIN AND T. A. GENKE. *Ibid.* 374-5.—L. Gurvich's formula (*C. A.* 8, 2090) for ordinary (positive) adsorption, $X = 100(c - c')/(100 - c')$, in which $X = g.$ of solute adsorbed from 100 g. of soln., $c =$ concn. before and $c' =$ concn. of solute after adsorption, is changed into the form $X = 100(c' - c)/(100 - c')$ to express the change of concn. taking place in negative adsorption. Further the quantity of solvent absorbed in negative adsorption is calcd. as follows: let $X =$ quantity of solvent absorbed from 100 g. soln.; $p =$ vol. of soln. in cc.; $c =$ concn. of soln. before and $C =$ concn. after adsorption, then $X = p - (pc/C) = Mg$. Then the quantity of solvent absorbed from 100 cc. of soln. is calcd. as: $X = 100(M/p) - 100(C - c)/C$. For pure H_2O , where $c = 0$, $X = 100\%$. The theory of negative adsorption is to be developed further in subsequent publications. W. A. PERLZWEIG

Aqueous solutions. Origin of osmotic effects. CAMILLE GILLET. *Compt. rend.* 177, 257-8 (1923).—A note basing the phenomena of solns. on the presence of very reactive mono-hydral mols. These act as a gas and in soln. follow the gas laws. The osmotic pressure is proportional not to the no. of dissolved mols. but to the no. of mono-hydral mols. Solns are discussed on this basis also. A. E. STEARN

Fusion, solution and ionization. W. F. SHORT. *N. Zealand J. Sci. Tech.* 5, 43-5 (1922).—A short discussion in which these phenomena are considered as essentially the same and explained on the basis of radiation hypothesis. A. E. STEARN

The significance of displacement of equilibrium. ALBERT COLSON. *Compt. rend.* 177, 184-6 (1923); cf. *C. A.* 17, 2808.—In the derivation of the equation connecting concn. of a satd. soln., C , with temp. and heat of soln. p , $dC/C = 0.5(dT/T)p$, the vol. of the solute has been neglected. In very concd. solns., this leads to discrepancies, such that the variation of soly. with temp. is not always nor exclusively detd. by the heat of soln., even under const. pressure. B. H. CARROLL

The allotropic change of ammonium nitrate at 32°. (A verification of Le Chatelier's law of solubility.) P. MONDAIN-MONVAL. *Compt. rend.* 177, 175-8 (1923).—Le Chatelier (*Compt. rend.* 130, 1606 (1900)) proved that at the transition point of a salt, the following relation holds between ds and ds' , the changes in soly. of the two forms for the same rise in temp., and L and L' , the resp. mol. heats of soln.: $ds/ds' = L/L'$. The soly. of NH_4NO_3 was detd. from 26 to 39°, by evapn. of the solns. At the transition point, 31.8°, $ds/ds' = 1.17$. Heats of soln. were detd. as described in *C. A.* 17, 1572. L at 28° = -2.93; L' at 36° = -2.53; $L/L' = 1.16$. B. H. CARROLL

Theories of reaction velocity. W. ADRIANI. *Chem. Weekblad* 18, 579-83, 613-5 (1921).—A. reviews the well known older theories of reaction velocity, the recent theory of Perrin (*C. A.* 13, 3067) and its criticism by Langmuir (*C. A.* 15, 798). R. BEUTNER

The vapor pressure of mixtures of hydrochloric acid and water. N. YANNAKIS. *Compt. rend.* 177, 174-5 (1923).—The total and partial pressures at 50° for a series of solns. of HCl in water were measured by the method of v. Zawidzski (*Z. physik. Chem.* 35, 129 (1901)). A pressure regulator was employed, and bumping prevented by a minute current between 2 electrodes at the bottom of the vessel. In the table given are the % HCl in soln. and vapor, resp., and the corresponding total pressures: 0, 0.92; 6.6, 0.07, 81; 10.3, 0.17, 75.5; 13.1, 0.34, 71; 17.1, 2.4, 63; 19.1, 4.5, 59; 19.2, 5.3, 58; 22.8, 18.6, 53; 23.6, 23.1, 52.5; 25.1, 35.6, 54; 28.7, 87.3, 85. B. H. CARROLL

Demonstration of molecular magnitudes in teaching. H. HERMANN. *Z. math. naturw. Unterr.* 53, 77-81 (1922).—Physik. Ber. 3, 1099-1100.—Kohlrausch's method using Stokes' law is employed. For the detn. of the velocity exponent in the liquid resistance formula, amber in water is best adapted. With increasing radius of particle (0.057-0.173 mm.) the deviation from Stokes' law decreases from 6% to 0.5%. Stokes' law is recommended as analogous to Ohm's law. Measurement of migration velocity

of ions is made according to the directions of Schaffer (Progr. d. Oberrealsch., Hamburg-Uhlenhorst, 1904). A U-tube is partly filled with a mixt. of equal vols. of 0.5 N CuSO_4 and 0.5 N $\text{K}_2\text{Cr}_2\text{O}_7$. Over this a layer of H_2SO_4 of equal cond. (1.324°) is poured. The dimensions of the app. were: length of colored liquid 50 cm., distance between electrodes 80 cm., vol. of colored liquid 43 cc. In 9 min. the Cu ions had gone 0.5 cm. at a current strength of 0.3 amp., giving a velocity coeff. of 9.27×10^{-4} cm./sec. and electro-friction of 5.6×10^{11} dynes. Stokes' law yields an ionic radius, then, of the order of 10^{-8} cm.

Catalysis and catalysts. S. P. SÄDILER, *Am. J. Pharm.* **95**, 270-85 (1923).
A popular lecture.

Promotion of catalytic reactions. I. SAMUEL MIDDSFORTH, *J. Chem. Soc.* **123**, 1452-69 (1923).—1. The action of H_2 on CO and CO_2 . The CO was 99.8% pure. The H_2 was electrolytic and 99.9% pure. CO was used directly from cylinders. The catalyst, Ni , was deposited from purified salts on purified pumice in the proportions 0.1 g. of reduced Ni to 1 g. of pumice. The reactions involved were $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ and $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$. To provide an excess of H_2 , the proportions used were $\text{H}_2:\text{CO}::5:1$ and $\text{H}_2:\text{CO}_2::6:1$, by vol. The max. catalytic effect was measured by the max. speed at which the mixed gas could be passed over the catalyst and promoter with almost complete removal of the CO or CO_2 . The reaction chamber was a straight tube fused to a preheating coil which surrounded it. The several promoters associated with 0.1 g. of Ni on 1 g. of pumice in the order of decreasing efficiency in accelerating the speed of the gaseous reactions are as follows: Ce , Th , Be , Cr , Al , Si , Zr , Mo , V oxides (Sn and Mg oxides, Cu and Ag produce no acceleration). The formation of CH_4 from H_2 and CO or CO_2 probably consists in the formation of intermediate addn. products of the MeOH type followed by the splitting off of water. The CH_2 resulting is immediately hydrogenated to CH_4 . Or a complex intermediate product, H_2NiCOH_2 , forms and decomposes into Ni , CH_4 and H_2O . In either case Ni must catalyze by acting as both a hydrogenating agent and as a dehydrating agent. It is not a good agent for the latter process. The substances which promote its catalytic action are good dehydrating agents. When $\text{CH}_3\text{OH} + 3\text{H}_2$ is passed over Ni the decompn. into CO and H_2 is much more rapid than the formation of CH_4 and H_2O . If thoria be added the rate of formation of CH_4 is increased fourteenfold. When Fe catalyzes the interaction of CO and H_2O to form CO_2 and H_2 the most effective promoters are O carriers and hydrating agents. This indicates that H_2 is produced through the formation of formic acid as well as by alternate oxidation and reduction. The oxidation of a gas in a gas mantle may be considered to consist of the addn. of O_2 to form an intermediate compd. and its subsequent dehydration. The catalyst should be a powerful O carrier and a strong dehydrating agent. The promoter acts (1) by decomposing intermediate compds. formed by the catalyst, or (2) by causing substances to combine, or (3) by adsorption to increase concn. Promoters may act selectively.

The contact effect of charcoal in oxidative reactions. A. G. DOROSHEVSKII AND G. S. PAVLOV, *J. Russ. Phys. Chem. Soc.* **49**, 1, 169-75 (1917); cf. *C. A.* **11**, 3171. Charcoal from birchwood was satd. in the desiccator with CS_2 . This led to the production of free S adsorbed on the charcoal. Then a definite amt. of Na_2CO_3 in soln. was added and the mass dried at 100° . During the process of drying the S was partly oxidized to SO_4 , and it was completely oxidized when a current of warm moist air was passed through the mixt. The final amt. of SO_4 so produced was conditioned by the quantity of Na_2CO_3 present. The intermediate production of Na_2SO_3 and its subsequent oxidation under the influence of the charcoal to Na_2SO_4 is supposed. With charcoal from sugar similar results were obtained. The study of the mechanism of the oxidation of CS_2 in the presence of charcoal led to the following conclusions: Charcoal adsorbs CS_2 with evolution of heat; in the presence of excess of air or O_2 more heat is eliminated and a considerable amt. of free S is produced. The charcoal then regains much of its initial adsorptive capacity for CS_2 . Birchwood charcoal was found to be much more effective in this oxidative process than sugar charcoal. Furthermore it was shown by the authors that the oxidation of $\text{SO}_2 + \text{O} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$ can be very successfully catalyzed by charcoal. The SO_2 was adsorbed on the charcoal to satn., O_2 was introduced under pressure in several small portions, the liberated SO_4 absorbed by added H_2O , and the process repeated until all of the SO_2 was completely oxidized. Quant. measurements are given.

The equilibrium of the reciprocal system sodium chloride magnesium sulfate in application to natural brines. N. S. KURNAKOV AND S. F. ZHEMCHUZHNIK, *J. Russ. Phys. Chem. Soc.* **51**, 1, 1-59 (1920).—In addn. to the data previously published (*C. A.*

17, 2220) the following observations were made: The isothermic diagram of the equilibria of the reciprocal system NaCl-MgSO_4 is characterized at 0° by 4 and at 25° by 7 surfaces or fields of crystn., resp., corresponding to the sepn. of similar nos. of solid phases. The fields of crystn. represent graphically the sepn. of NaCl , MgSO_4 , ternardite, astrachanite and of the other salts obtained on the evapn. of the sea waters of the Aral-Caspian region. The fields of crystn. are detd. by the trajectories of crystn. issuing from one point—the pole of the given field. With changing temp. the poles of isothermic fields travel along straight lines or axes whose positions are invariable in the diagrams under varying conditions of the systems. The isotherm of satd. solns. is a closed topological complex delimited by one border line. Upon the removal of a definite no. of linear segments a closed complex becomes open and is subsequently changed into a compd. and a simple tree of crystn. The end or "eutonic" point of the crystn. tree is common for all the paths of crystn. of the given diagram. This point in the isothermic system is analogous to the eutectic point in a temp. of fusion diagram. The connection existing between the theory of chem. equilibria and the algebraic theory of end groups is also discussed.

W. A. PERLZWEIG

Internal friction of the systems water-bromal and chloral-dimethylethylcarbinol. N. N. EFRIMOV. *J. Russ. Phys. Chem. Soc.* 50, 1, 338–71 (1918).—This article contains additional data to the studies made by N. Kurnakov and his collaborators (*J. Russ. Phys. Chem. Soc.* 44, 375; *Z. physik. Chem.* 85, 401; and *C. A.* 7, 1126, 2147; 9, 11, 2478) on the isothermic viscosity curves of various binary systems. The isotherms of viscosity in the system $\text{CBr}_3\text{CHO-H}_2\text{O}$ are characterized by "irrational" maxima, i. e., max. points changing their positions with changes of temp., which indicates a considerable degree of dissociation of $\text{CBr}_3\text{CH}(\text{OH})_2$ in the liquid phase. The heat of fusion curves of this system indicates the possibility of only 1 reaction between the 2 components yielding the normal bromal monohydrate. The b. p. of this system reaches a min. within the range of mol. concn. of 35–45% CBr_3CHO . Mixts. of $\text{CBr}_3\text{CH}(\text{OH})_2$ with H_2O and with anhyd. CBr_3CHO are easily dehydrated on warming which causes the appearance of 2 layers in liquid solns. The properties of the system $\text{CCl}_3\text{CHO-(CH}_3)_2\text{COHC}_2\text{H}_5$ (which is regarded as a chloral alcoholate) are similar to those of $\text{CCl}_3\text{CHO-H}_2\text{O}$ and of $\text{CCl}_3\text{CHO-EtOH}$. In the liquid phase this system exists in a state of greater or lesser dissociation, as is shown by the character of the viscosity isotherms and of the curves of the temp. coeff. of internal friction.

W. A. PERLZWEIG

Molecular compounds of phosphoric acid and ether. MARK RABINOWITSCH AND SOPHIE JAKUBSOHN. *Z. anorg. allgem. Chem.* 129, 55–9 (1923).—The investigation of this system between 0 and 17.5% ether by the method of thermal analysis, reveals the existence of two compds.: $6\text{H}_3\text{PO}_4 \cdot (\text{C}_2\text{H}_5)_2\text{O}$, m. p. 28.2° ; and $4\text{H}_3\text{PO}_4 \cdot (\text{C}_2\text{H}_5)_2\text{O}$, m. p. 30° .

J. A. ALMQUIST

Binary critical solution temperatures as criteria of the purity of acetic acid. D. C. JONES. *J. Chem. Soc.* 123, 1374–84 (1923).—The presence of H_2O in AcOH raises the crit. soln. temps. The rise is almost linear in the binary systems AcOH-petroleum , AcOH-cyclohexane , and AcOH-CS_2 . When sufficient H_2O is present to lower the m. p. of AcOH 1° , the change in crit. soln. temp. was (a) for AcOH-petroleum 16° , (b) for AcOH-cyclohexane 8.4° , (c) for AcOH-CS_2 6.9° . This relationship furnishes an extremely delicate method for estg. the concn. of H_2O in AcOH .

F. E. BROWN

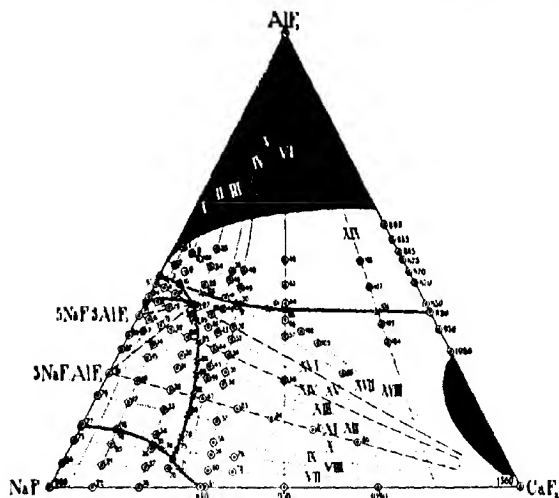
Ternary critical solution temperatures as criteria of liquid purity. D. C. JONES. *J. Chem. Soc.* 123, 1384–95 (1923).—The crit. soln. temp. is generally very distinct. By suitably selecting 2 of the components and adjusting their concns. it is possible (1) to apply this method to a large no. of liquids and (2) to bring the miscibility point within any convenient range of temp. Aq. solns. of AcOH constitute a good solvent for nearly all stable org. liquids. A rise of as much as 45° in the crit. soln. temp. is caused by as little as 1% impurity. Tables or graphs are given for cyclohexane, nitrobenzene, *p*-nitrotoluene, thiophene and CS_2 used separately with aq. AcOH .

F. E. BROWN

Critical solution temperature for solids in the binary system ammonium chloride-manganous chloride dihydrate. F. W. J. CLENDINNEN AND A. C. D. RIVETT. *J. Chem. Soc.* 123, 1344–51 (1923).—There is an analogy between a solid-solid two-phase system and the two-phase liquid-vapor system similar to that between a liquid-liquid two-phase system and a liquid-vapor system; i. e., there is a crit. soln. temp. This may be an upper or a lower crit. soln. temp. The system $\text{NH}_4\text{Cl-MnCl}_2 \cdot 2\text{H}_2\text{O}$ was investigated at 70, 60, 50, 40, 32.5, 25, 20, and 10° . D. of the soln., compn. of the soln., and compn. of the crystals sepg. out are given for more than 100 different conditions of temp. and compn. The data and the curves plotted from them show that there is a lower crit. soln. temp. for this mixt. at a point a little below 25° .

F. E. BROWN

Fusibility of the ternary system: sodium fluoride, calcium fluoride, aluminium fluoride. P. P. FEDOTIEFF AND W. P. ILJINSKY. *Z. anorg. allgem. Chem.* 129, 93-107 (1923).—The results of the study are given in the accompanying diagram. The black



portions denote the unrealizable regions. The invariant points occur at 780, 705 and 675°.

J. A. ALMQUIST

Research on the ternary eutectic points of the systems: resorcinol, α -nitronaphthalene, pyrocatechol; hydroquinone, resorcinol, pyrocatechol; hydroquinone, α -nitronaphthalene, pyrocatechol. PIERRE SENDEN. *Bull. soc. chim. Belg.* 32, 281-5 (1923).—The ternary eutectic point (detd. in the usual way) of the first system is at 37.5° with 15% resorcinol, 65% nitronaphthalene and 20% pyrocatechol; the eutectic point of the second system is at 46.0° with 10% hydroquinone, 45% resorcinol and 45% pyrocatechol; the one of the third system is at 48° with 3% hydroquinone, 88% nitronaphthalene and 9% pyrocatechol.

R. BEUTNER

Systematic affinity principle. XXI. The amines of the halides of bivalent tin. WILHELM BILTZ AND WILHELM FISCHER. *Z. anorg. allgem. Chem.* 129, 1-14 (1923); cf. C. A. 17, 2682.—Following are the compds. formed by the stannous halides with NH_3 (new ones in italics), together with the temps. for vapor pressures of 100 mm. and the heats of dissoc. (Q) in kg. cal. per mol. of NH_3 : $\text{SnCl}_2 \cdot 2\text{NH}_3$, -55°, 7.6; 4NH_3 , -15°, 9.3; $\text{SnBr}_2 \cdot 2\text{NH}_3$, -57°, 7.55; 5NH_3 , -2°, 9.8; 3NH_3 , 86°, 12.4; 2NH_3 , 102°, 13.6; $\text{SnI}_2 \cdot 10$ or 9NH_3 , -48°, 7.9; 5NH_3 , 10°, 10.2; 3NH_3 , 55°, 11.9; 2NH_3 , 94°, 13.3; 1NH_3 , 157°, 16.0. The total heats of formation as detd. tensimetrically and calorimetrically agree closely. The latter method involves measurement of the heats of soln. of the Sn halides and of the amines in 1% HCl. The values are +0.8 cal. for SnCl_2 , -1.6 cal. for SnBr_2 , and -5.8 cal. for SnI_2 . The possibility of the formation of 2 shells of NH_3 around a central cationic metal is again postulated to account for combination with more than 6 mols. of NH_3 . XXII. The heats of formation of intermetallic compounds. WILHELM BILTZ AND CARL HAASE. *Ibid.* 141-60.—The heats of formation of 12 intermetallic compds. are measured by exptly. detg. in the calorimeter the differences between the heats of soln. of the compds. and of the uncombined constituent metals. In addn. the ds. of the compds. are detd. in order to calc. % contractions in formation from the elements as possible parallel phenomena to heats of formation. Following are the data, the first no. representing the heat of formation in kg. cal. and the second the percentage contraction: Mg_2Al_3 , 49, 3.5; FeAl_3 , 25, 5.1; Mg_2Ca , 43, 4.5; Mg_2Cd , 9.2, 5.9;

Na_2Hg , 12.9, —; NaCd , 8.5, 11.8; NaCu , 12.4, 6.7; SbCd , 3, —7.4; SbCu , 4, —9.0; Cu_2Sb , 2.3, 10.1; Cu_2Cd , —1.3, 3.4. Such a parallel does not exist, therefore. It is shown that the heats divided by the no. of atoms in the mol. give a series of nos. in the order to be expected from the position of the metals in the electromotive series. **XXIII. The amines of the zinc halides.** WILHELM BILTZ AND CARL MESSERKNECHT. *Ibid* 161–75.—A study of the isotherms in the same way as used previously in this series, and calorimetric measurements, lead to the following values for the *partial heats of dissociation* in kg. cal. per mol. of NH_3 (from a given ammine to the next lower definite compd.), and the *total heats* (complete removal of NH_3 from a given ammine), resp. $\text{ZnCl}_2 \cdot 10\text{NH}_3$ (new), 7.07, 11.75; 6NH_3 , 10.7, 14.9; 4NH_3 , 11.82, 17.0; 2NH_3 , 19.2, 22.1; (1NH_3), —, 25.0; $\text{ZnBr}_2 \cdot 6\text{NH}_3$, 11.02, 15.5; 4NH_3 , 13.55, 17.8; 2NH_3 , 19.9, 22.0; (1NH_3), —, 24.1; $\text{ZnI}_2 \cdot 6\text{NH}_3$, 10.93, 15.7; 4NH_3 , 15.38, 18.0; 2NH_3 , 19.42, 21.0; (1NH_3), —, 22.0. The total heats of dissoc. (or formation) are used to construct the valence isobars instead of the usual temps. for a common vapor pressure. The anion effect runs $\text{Cl} < \text{Br} < \text{I}$ for the compds. with 6 and 4 NH_3 , and $\text{Cl} > \text{Br} > \text{I}$ for those with 2 or 1 NH_3 . It is indicated that the discovery of $\text{CoCl}_2 \cdot 10\text{NH}_3$ by Clark (*C. A.* 15, 456) has been verified following the isolation of the decamine of ZnCl_2 . G. L. CLARK

The third principle of thermodynamics and some of its consequences. A quantitative application of Berthelot's principle. VL. A. KISTYAKOVSKII. *J. Russ. Phys. Chem. Soc.* 53, 1, 247–55(1921).—A quant. formulation of Berthelot's principle of *maximum work* was made which permits of broad applications to the detn. of such quantities as the heat of transformation, the free energy of compds., etc. A restatement of Berthelot's principle is briefly given as: "For every transformation of substances, chem. or phys., a characteristic point may be found by varying the temp. and pressure at which point $A_1 = Q_1$, i. e., the free energy = the heat of transformation, and at the same time $dA/dT = 0$, or, when the 1st deriv. of the free energy to the temp. (the temp. coeff. for the given point) is also = 0." Nernst's theorem presents a special case of the above postulate, namely where $T = 0$. The application of the above principle also leads to the equation $q = T(dA/dT)$, where q is the heat of the side process accompanying the chem. reaction. This leads to the condition in which with small increase in temp. Q becomes either greater or less than A . By using the last equation the temp. coeff. of galvanic elements can be calcd. from the heats of fusion of ice and Hg. It also gives a simple formula for the latent heat of vaporization of poorly associated liquids (cf. following abstr.). The general problem of the max. work which can be obtained from any given reaction is discussed. W. A. PERLZWEIG

Latent heat of vaporization. VL. A. KISTYAKOVSKII. *J. Russ. Phys. Chem. Soc.* 53, 1, 256–64(1921).—A new formula for the calcn. of the heat of vapn. of unassociated liquids was worked out by applying the 3rd principle of thermodynamics (cf. preceding abstr.). The formula is $JQ = RT \ln RT$, which states that for unassociated (or poorly associated) liquids, whose vapors at the b. p. have the normal mol. wt., the heat of vapn. = the vol. of the vapor multiplied by the natural log of the same vol. J is the mech. heat equiv. in joules, Q is in large cal., the gas pressure is in atm. and the vol. in cc. Satisfactorily agreeing values for Q were calcd. by the use of this formula for 74 poorly associated liquids which includes all of those given in Landolt-Börnstein *Phys. Chem. Tabellen*, 1912, 834–42, in addn. to some others of previous Russian data. The new formula does not contain any empirical factors and it is offered by K. as the law of the latent heat of vapn. for unassociated liquids at their b. ps. and at 1 atm. pressure. W. A. PERLZWEIG

The question of the heat of recrystallization. J. A. M. VAN LIEMPT. *Z. anorg. allgem. Chem.* 129, 263–4(1923).—L. has attempted to det. the magnitude of the heat of recrystn. by measuring the difference in the heats of combustion of unworked and cold drawn W. The measurements were made in a Mahler bomb calorimeter. The difference in heat of combustion of the 2 was less than the error of the detn. This agrees with the measurements of Koref and Wolff, who could find no difference in the heats of soln. of cold drawn and recrystd. W. There is therefore no thermally detectable difference in the heat of recrystn. of W. L. T. FAIRHALL

Heat effect of isomorphous mixture formations. N. N. NAGORNOV. *J. Russ. Phys. Chem. Soc.* 51, 301–10(1919).—Fine pulverized frozen melts of (1) $\text{C}_6\text{H}_5\text{CH}=\text{CCl}_2\text{CHO} + \text{C}_6\text{H}_5\text{CH}=\text{CBr}_2\text{CHO}$, (2) $\text{C}_6\text{H}_5\text{Cl}_2 + \text{C}_6\text{H}_5\text{Br}_2$, (3) $\text{C}_6\text{H}_5\text{Cl}_2 + \text{C}_6\text{H}_5\text{ClI}$, (4) $\text{C}_6\text{H}_5\text{Br}_2 + \text{C}_6\text{H}_5\text{I}$, (5) $\text{C}_6\text{H}_5\text{I} + \text{C}_6\text{H}_5(\text{NO}_2)_2$ were dissolved in benzene, and the heats of dissoln. compared to those calcd. from the dissoln. heats of the pure compds. and also to those obtained for plain mixts. of the pulverized substances. Sp. heats of the obtained solns. were detd. by sending a current through a manganin resistor, immersed in the benzene, and taking the temps. Results: series (1) completely iso-

morphous, formation heats negative; series (2) same, but larger effects per mol.; series (3) same, but liquidus has a min., and the effects are still much larger; series (4) no isomorphous mixts., no heat effect of eutectic formation; series (5) no isomorphous mixts., but an equimol. compd., heat of formation negative, moderate. Conclusions. Analogously to the cases of isomorphous mixts. of inorg. salts, those of org. substances will generally show a negative heat effect of formation, the value of it being the larger, the more concave the liquidus to the concus. line. Positive values can be expected for liquidus either with a max., or very convex at least.

The lattice energy and dimensions of mixed crystals. H. G. GRIMM AND K. F. HERZFELD. *Z. Physik* **16**, 77-83(1923). By means of the crystal lattice theory of Born and Landé it is possible to calc. the heats of formation of mixed crystals if the lattice interplanar distances are known. The formula derived is $Q = [u_0/b(1 + \gamma_n x)^n] - [x(u_0/a)] - [(1-x)(u_0/b)]$, where a and b are the lattice distances of the pure components, x is the mol. fraction, n is an integer, $u_0 = Ne^2\alpha(1 - 1/n^2)(N - 1)$ pairs of cations and anions, e = charge, α = Madelung potential, n^2 = power of repulsion potential, and $\gamma_n = (u_0/b)^{1/n} - 1$. Results so obtained for KCl-KBr, KCl-KI, KBr-KI, NaCl-KCl, NaBr-KBr are compared with Q exptl. measured and found to agree fairly well. These heats of formation are small and the negative sign explains the decompn. of mixed crystals with decreasing temp. Agreement between calcd. and exptl. values is best if the empirical rule of the additivity of mol. vols. in mixed crystal formation is used in calcn. of lattice distances.

The thermodynamics of mixed crystal formation. K. F. HERZFELD. *Z. Physik* **16**, 84-90(1923).—A continuation of the preceding paper making use of entropies. Numerous formulas are mathematically deduced which govern all mixed crystal phenomena except the melting curve. By means of them the miscibility, crit. sepn. points, etc., may be detd. Since the heat of formation of mixed crystals is negative, a completely disordered arrangement of particles is indicated. An hypothesis of double salt formation, in which these are considered true chem. compds. in the solid state, is presented very briefly.

The question of energy at zero absolute. KURT BENNEWITZ AND FRANZ SIMON. *Z. Physik* **16**, 183-199(1923).—From quantum theory considerations it is concluded that the low m. p. of H indicates with considerable probability the existence of energy at the abs. zero. The large deviation of the low-boiling gases from Trouton's rule also indicates the presence of energy at abs. zero.

The theory of induced alternate polarities in a chain of atoms. ARTHUR LAPWORTH AND ROBERT ROBINSON. *Trans. Faraday Soc.* **1923** (preprint). This is a crit. discussion of papers by L. (C. A. **16**, 2017), R. (C. A. **16**, 2233), and T. LOWRY (C. A. **17**, 913).

Electrolytic conduction: sequel to an attempt (1886) to apply a theory of residual affinity. H. E. ARMSTRONG. *Proc. Roy. Soc. (London)* **103A**, 619-21(1923). It is suggested that the explanation of the behavior of a salt in electrolysis is to be found in its structure, and that often complex mols. of the salt are present and play an important part in the process. The apparent carrying of the current by the metallic ions in the electrolysis of Ag halides and by non-metallic ions in the case of Pb halides is explained on this theory.

The dielectric strength of gases, liquids and solids. A. GUNTHER SCHULZE. *Helios* **28**, 397-403, 409-11(1922); *Physik. Ber.* **3**, 1153; cf. C. A. **17**, 671. For gases, from considerations of field strength, electrode shape, retardation, curve form and frequency of a.c., pressure, magnetic field, etc., the conclusion is drawn that for large electrode distances and high voltages the results of different workers vary so widely that an exact knowledge of voltage and sparking distances cannot be spoken of. For liquids, the influence of impurities is very great as well as those factors mentioned under gases. For solids, the forms of electrodes free from objection constitute the greatest problem. A differentiation is made between genuine dielectrics, which contain very few ions and can be recognized by being good dielectrics in the molten state (as paraffin), and pseudo-dielectrics, where ionic structure is present but ionic friction in the solid state at ordinary temps. is very great (as glass, porcelain, marble, etc.). For gases the theory of dielectric strength is satisfactory only in its bare fundamentals; for liquids there is no knowledge as yet of the relation between dielectric strength and structure; and for solids the state is even worse. In short the largest part of the work in this important field is yet to be done.

The electrical conductivity of solid $2\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$. MARK RAHINOWITSCH. *Z. anorg. allgem. Chem.* **129**, 60-6(1923).—R. studied the cond. of $2\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ in the cryst. and supercooled states. The ratio of these conds. at comparable temps. is taken as a

measure of the "degree of loosening" (cf. C. A. 16, 3797). The order of magnitude of the sp. cond. for the crystals is 10^{-4} ; for the supercooled hydrate 10^{-3} . The temp. coeff. is positive. The decrease in the cond. of anhyd. H_3PO_4 with time is connected with some change in the H_3PO_4 .

J. A. ALMQUIST

The movement of drops of mercury under the influence of an electric current. A. FRUMKIN. *J. Russ. Phys. Chem. Soc.* 49, 1, 207-10(1917).—Christiansen had previously shown (*Drud. Ann.* 12, 1072(1903)) that if a drop of Hg be positively charged in relation to a soln. through which it is falling, and, if an elec. current be passed through the soln., then the falling drop will be deflected from its vertical path towards the cathode. If the Hg drop be negatively charged in relation to the soln., then the deflection will be towards the anode. F. utilized this observation for detg. the "zero" soln., i. e., the soln. in which the Hg drop has the max. surface tension, and the p.d. of the Hg in relation to such soln. = 0. The method employed consisted of adding increasing amts. of $HgCl_2$ or KCN to a 0.01 N KCl soln. and measuring the deflection of falling Hg drops in each soln., also the e. m. f. of the chain $Hg|soln. studied|0.01 N KCl + HgCl_2|Hg$. The measurements were made in a special app. in an atm. of H_2 after establishing a const. e. m. f. of the system, without the Hg, satd. with H_2 . The Hg drops were introduced from a fine-tipped buret and had a diam. of 2.2 mm.; the current used was 0.001-0.003 amp., and the deflection of the path of the drops was observed by means of a scale placed within the vessel. 0.01 N KCN and 0.0-0.0002 N $HgCl_2$ solns. were studied. Under the conditions of the expts. the p.d. of the chain did not vary more than 2-3 milliv. With + signifying deflection towards cathode and — towards anode, the following deflections were observed at the following potentials: 0.620 v. +; 0.635 +; 0.636 +; 0.644 —; 0.650 —; 0.660 —. From this it is concluded that with a 0.01 N electrode the zero point lies in the vicinity of 0.640 v., and at 0.586 v. for 0.1 N electrode. This agrees well with Palmer's value of 0.572 v. for a 0.1 N KCN electrode (C. A. 1, 2527).

W. A. PERLZWEIG

Optical constants of certain liquids for short electric waves. J. D. TEAR. *Phys. Rev.* 21, 611-22(1923).—Optical consts. of H_2O , glycerol, Me and Et alcs. were measured for elec. waves of from 4 to 27 mm. length. This was possible through the new technic for generating and detecting these waves recently developed by T. The extinction and reflection coeffs. were measured, and the values of n were then computed by the Cauchy-Quincke formula. Water shows absorption max. at wave lengths of 20.7, and perhaps 2 mm.; its index drops from 8.7 at 40 mm. to 5.3 at 4 mm. The exptl. values agree with those computed by Rubens from the Debye theory for wave length greater than 40 and less than 0.2 mm. The discrepancies in the intermediate region are evidently due to the presence of 2 or 3 absorption bands where only 1 had been assumed.

L. B. LOEB

Optical phenomena caused by anisotropic molecules. H. H. BUZEMAN. *Diss. Groningen* 72 pp.(1922) (Hollandisch); *Physik. Ber.* 3, 1348.—Mathematical. Light-scattering and the electro-optic Kerr effect are studied. A difference in scattering by liquids and gases must be considered since the former are considered homogeneous and the latter not so. The intensity relation between the incident beam and the scattered light in liquids gives a magnitude which is a measure of their anisotropy. For gases this measure is found in the intensity relation between 2 components of the scattered light polarized perpendicular to each other. The dielec. const. and the Kerr const. lead to the assumption that the mols. are not only anisotropic but also have elec. dipoles with unvarying moment. It is possible occasionally to det. the dipole moment, and then, with the aid of the const. of anisotropy found by the scattering effect, to ascertain the Kerr const. The correspondence with the theoretical values when so detd. is not always satisfactory.

A. E. STERN

Double refraction of solutions of dyes. H. FREUNDLICH, C. SCHUSTER and H. ZOCHER. *Z. physik. Chem.* 105, 119-44(1923).—Sols. of benzopurpurin, prepd. by warming the dye with H_2O , become double refracting on cooling if they are sufficiently concd. Below a dye concn. of 0.35% double refraction does not appear even after an elapse of several weeks. In these dil. solns., however, double refraction can be developed by the addn. of electrolytes. The occurrence of double refraction in dil. solns. of benzopurpurin, under the influence of different electrolytes, has been studied. The nature of the anion has but little influence on the phenomenon; the cation plays the decisive role. As in the process of coagulation, the valence of the ion is a detg. factor: inorg. univalent cations (Li^+ , Na^+ , Rb^+ , NH_4^+) exhibit, in a 0.25% sol, an optimum of action at about 40 millimols. per l., inorg. bivalent cations (Mg^{++} , SR^{++} , Ba^{++} , Cd^{++}) such at about 0.2 millimol. per l. These concns. are considerably lower than those at which the sol becomes turbid (about 110 millimols. for the univalent and 1.0 millimol. for

the bivalent cations). With univalent and trivalent org. cations the optimum for the appearance of double refraction and the turbidity point lie very close together. Although with inorg. cations an optimum of action exists at 40 millimols. per l., between 60 and 80 millimols. there is a region of very much less activity; with inorg. bivalent cations such a region lies between 0.3 and 0.7 millimol. per l. The Tyndall cone, which the sol shows in the ultramicroscope, does not exhibit a similar behavior. It increases uniformly with increasing concn. of electrolyte. Colloids like gelatin and albumin behave as protective colloids and prevent the appearance of double refraction within a definite range of concn. At higher concns. gelatin exerts first a sensitizing and then a protective action on the turbidity. In double refracting sols contg. electrolyte, double refraction disappears on warming. A definite transition point exists; below this temp. double refraction is still manifested even after several hours heating; above it double refraction disappears. The transition temp. depends upon the nature and concn. of the electrolyte present, the age of the sol and its previous treatment. This temp. is lower for Li^+ and Na^+ ions, higher for K^+ and NH_4^+ ions, considerably higher for Mg^{++} and Ba^{++} ions, and increases markedly with increasing concn. of the electrolyte and the time elapsing after the addn. of the electrolyte to the sol. The transition temp. is lowered by shaking the sol with glass beads. The behavior at the transition point can be regarded as a peptization. The foregoing facts make it probable that the appearance of double refraction in benzopurpurin sols results from the development of longer particles which are formed by an ordered coagulation. This must be differentiated from the ordinary unordered coagulation. The optimum of the appearance of double refraction probably results from the unordered coagulation predominating over the ordered coagulation at higher concns. of electrolyte. The ultramicroscope shows the presence of long particles in concd. benzopurpurin sols. In dil. sols, it is not possible to distinguish between double refracting and non-double refracting sols by means of the ultramicroscope. In the double refracting sols the presence must be assumed of amionic particles which are formed by ordered coagulation from amionic primary particles. Under similar conditions cotton-yellow gives double refraction like benzopurpurin, only the tendency to ordered coagulation is greater and consequently the process proceeds more rapidly. As with benzopurpurin, a characteristic optimum has been observed for cotton-yellow with certain electrolytes.

H. J. CREIGHTON

Demonstration of the double refraction due to motion of a vanadium pentoxide sol, and some applications. R. H. HUMPHRY. *Proc. Phys. Soc. London* 35, 217-8 (1923).—The double refraction is due to the formation of rod-shaped particles which set themselves in a definite direction when the liquid is caused to move. The applications demonstrated were: (1) deviation from rectilinear flow owing to the presence of an obstacle (the nicols being set perpendicular to and parallel to the stream); (2) thermal convection stream from an elec. heated wire (nicols set at 45° to the direction to be investigated in this and next two cases); (3) efflux of liquid from a jet below the surface; (4) disturbance caused by the fall of a liquid globule of nearly the same d. through the sol.; and (5) disturbances below the surface due to surface forces when a drop of alc. is placed on the surface. The method of prep. the sol is described in detail.

C. C. VAN VOORHIS

Investigation of a general and uniform application of the quantum theory, and a quantum theory of dispersion. ADOLF SMEKAL. *Wiener Anz.* 1922, 79-81; *Physik. Ber.* 3, 1104-5.—The applications have hitherto been confined to isolated systems whose mutual influences are described by classical laws. In this paper these effects are subjected to quantum laws; and the motions of all positive and negative elementary charges of any portion of space are suggested as the main single quantum problem. For such problems, that quantum method was used which permitted a development in multiple Fourier's series after a finite no. of independent periods. This is in contrast to the present conception—the application of the Schwarzschild form of the quantum hypothesis to any particular soln. of the equations of motion. This conception of mutual effect does not modify the present applications of the theory very much. The frequency of the newly introduced intermol. quantum constraints are of another order of magnitude than the frequency of isolated systems as considered up to now, and come into importance as a broadening of spectrum lines, dispersion and diffraction. This concept makes possible a general quantum explanation of all spectral phenomena including continuous spectra and heat radiation. The theory of reaction velocity is also related.

A. E. STEARN

The specific heats of gases and vapors. AIMÉ WITZ. *Rev. gén. sci.* 34, 425-35 (1923).—A rather elementary historical and critical review of the subject. W. P. W.

Electron theory of valency applied to coordination compounds (SPIERS) 6. Salt solutions and their graphic representation (LAADÉ) 18. Solubility. VIII. Solubility of Co amines (EPHRAÏM) 6. Pectin-sugar-acid gels (SUCHARIPA) 12. A critical search for a heavier constituent of the atmosphere by means of the mass-spectrograph (ASTON) 3. Possible error in the theory of coordination (LOWRY) 6. Catalytic reduction and hydrogenation (ANDERSON) 10. Solubility of KClO_3 in aqueous solutions of Na_2CO_3 , of NaCl and of K_2CO_3 (ALEKSEEVSKII) 4. Germanium. VI. Metallic Ge. Reduction of GeO_2 . Preparation of fused Ge. Physical and chemical properties (DENNIS, *et al.*) 6. Some moisture relations of colloids (FISHER) 13.

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VENABLE, FRANCES: **History of Chemistry**. Boston, New York. Chicago: D. C. Heath & Co. 168 pp. \$1.60. Reviewed in *J. Am. Chem. Soc.* 45, 1854(1923).

3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

S. C. LIND

Phosphorescence caused by active nitrogen. W. JEVONS. *Nature* 111, 705-6 (1923).—E. P. Lewis (cf. *C. A.* 17, 2827) reported that active N excites phosphorescence in a no. of solid compds. J. has observed this with AlCl_3 , a compd. not in Lewis' list.

D. C. BARDWELL

The fluorescence and coloration of glass produced by β -rays. J. R. CLARKE. *Phil. Mag.* 45, 735-8(1923).—Three specimens of soda-lime glass of slightly different compn. were exposed to Ra Em until they were colored a deep brown and had ceased to fluoresce. The color was due to β -rays and extended only to their depth of penetration. The duration of fluorescence was quite uniform for all 3: at 110° , 13 mins; at 180° , 3 mins.; at 235° , 1.25 to 1.50 mins.; and at 350° , 0.5 to 0.75 mins. At 95° another specimen fluoresced for 15 hrs. It was estd. that decolorization, which was complete at all temps. when fluorescence was exhausted, would take place immediately at 500° to 600° . The annealing temps. of the 3 glasses were 526° , 538° and 562° , and it is concluded that coloration and decoloration are connected with a change in the state of mol. aggregation. Of 19 specimens which were colored, 14 were brown and 5 purple. Only those contg. Mn colored purple; the Na content appeared to have no influence.

S. C. L.

The orbit and the energy of a valence electron in heavy atoms. H. P. BERLAGE, JR. *Physica* 3, 206-12(1923).—A theoretical paper which is not adapted for abstracting.

C. C. VAN VOORHIS

Quantum theory and the structure of the atom and its radiation. I, II and III.

OLIVER LODGE. *Beams* 13, 10-9, 75-8, 148-57(1923).—An interesting semi-popular review.

Atomic projectiles and their properties. ERNEST RUTHERFORD. *Electrician* 91, 144-5(1923).—Cf. *C. A.* 17, 2818.

The electronic orbits in the excited helium atom. M. BORN AND W. HEISENBERG. *Z. Physik* 16, 229-43(1923).—On the assumption that one electron revolves around the He nucleus at a much greater distance from it than the other electron, all possible types of electronic orbits in the excited He atom are mathematically considered. The conclusion is reached that no explanation of the He spectrum can be obtained by the use of the usual quantum principles.

The field of gravitation of a spherical electron. H. L. VAN DER LINDEN. *Physica* 1, 190-7(1921).—Continuing the work of Nordström, Van den Bergh and others N. derives new formulas for the field of gravitation, using Einstein's equations.

Principles of the theory of quanta. P. S. EPSTEIN. *Proc. Acad. Sci. Amsterdam* 23, 1193-205(1922).—Planck's theory of the relativistic Kepler motion is examined on the basis of new considerations and found to be essentially correct. E. gives further developments which he tries to prove by means of Rutherford's observations on the colliding of α -particles and mols., especially by Rutherford's observation that the rays, produced by collision, move in the same direction as the α particles.

An explanation of the theory of the rotation of the atomic nucleus. III. HERBERT HENSTOCK. *Chem. News* 127, 18-21(1923).—H. applies his theory (*C. A.* 17, 2076, 2669, 2818) to the structure of oxides and peroxides. He gives a special structure for CO (and a similar one for SnCl₄, etc.) in which the C atom is an octahedron with one face opened out to a square, the O atom being a cube. Such distortions, and displacement of electrons from their normal positions to other corners of their cube, are assumed to occur in many double-bonded unions.

Bohr's model of the hydrogen molecules and their magnetic susceptibility. KÔ TARÔ HONDA. *Sci. Repts. Tohoku Imp. Univ.* 12, 123-5(1923).—Cf. *C. A.* 17, 673.

The model of the helium atom. H. A. KRAMERS. *Z. Physik* 13, 312-42(1923).—Correction of author name and reference in *C. A.* 17, 2077.

Separation of the isotopes of zinc. A. C. EGERTON AND W. B. LEE. *Proc. Roy. Soc. (London)* 103A, 499-515(1923); cf. *C. A.* 17, 674.—A partial sepn. of the isotopes of Zn, amounting to about 1 part in 1800 of d. [0.036 units of at. wt.] was obtained by a short series of distns. of molten Zn at very low pressure in a pyrex tube, an inner concentric tube cooled with water or liquid air being used as condenser. The efficiency of the operations was less than 50%, on the basis of Dempster's positive ray analysis of the isotopic compn. of Zn. The densities of the Zn samples (used as a measure of their at. wts.) were detd. by the method described by E. and L. (cf. *C. A.* 17, 3267). The av. results (densities at 16.3°) are: light fraction, 7.1381; ordinary Zn, 7.1400 (to within 1 part in 100,000); heavy fraction, 7.1420. The existence of a partial sepn. of the isotopes is highly probable, but not quite certain, as the individual detns. vary considerably. Impurities (only Fe and Pb were present in appreciable amts.) were shown by careful tests to be incapable of accounting for the observed changes in d. caused by distn.

Celtium or hafnium? ANON. *Chemistry & Industry* 42, 784-8(1923).—An editorial review of the evidence with the conclusion that Urbain should have the credit for the discovery of element no. 72 and the name celtium should be retained.

Color change and luminescence by radium rays. KARL PRZIBRAM. *Verh. Phys. Ges.* 3, 1-2(1922); *Physik. Ber.* 3, 852.—Discussion under the headings: excitement of luminescence by light and temp. increase, triboluminescence, photoelectric effect, color change, necessity in many cases of previous heating. By way of completing an earlier piece of work (*C. A.* 17, 2674), P. reports that orthoclase, adularia, scheelite and wolastonite, as previously observed with kunzite and fluorspar, show phosphorescence by light after exposure to Ra rays. In a phosphorescope uncolored kunzite shows phosphorescence lasting only a fraction of a second, while the colored material holds its property many minutes. In the latter material the entire spectrum from red to ultraviolet causes phosphorescence. The sharp difference formerly thought to exist between the effect of long and short wave lengths is not substantiated. Both kunzite and fluorspar, after exposure to Ra rays, show considerably increased triboluminescence.

An interpretation of radioactive disintegration on a quantum basis. ADOLF SMEKAL. *Wiener Anz.* 1922, 129-33; *Physik. Ber.* 3, 1105(1922).—While Bohr's postulates

permit, in principle at least, all quantum states of a chosen at. system to be detd. when the fundamental state is given, they say nothing of this latter. S.'s postulate, which considers mutual effects of different isolated atoms, is able in principle to reduce these basic states of atoms of different elements to that of one single element, *e. g.*, H. This requires that the changes of radioactive disintegration be explicable. That such is the case is shown by reference to the late researches of Meitner (*C. A.* 16, 3030) and Ellis (*C. A.* 16, 2071). The validity of the combination principle for γ -frequency of Ra B, as found by Ellis, proves the existence of a stationary quantum state for at. kernels. Contrary to English workers, it is assumed that β and γ line spectra are partly of a primary nature. Hence the existence of 2 types of quantum transfer follows, which result in γ -ray emission or the regular β -ray emission. A suggestion for the possibility of a similar explanation of the α -ray emission is given. A. H. STEARN

Distribution of the lengths of α -rays. IRENE CURIE. *J. phys. radium* 4, 170-84 (1923).—See *C. A.* 17, 1919. E. J. C.

The natural curvature of α -ray tracks. P. M. S. BLACKETT. *Proc. Camb. Phil. Soc.* 21, 517-20 (1923).—Shimizu and B. had independently reached the conclusion that towards the ends of the α -ray tracks the particles showed a pronounced tendency to curvature. The nature of this curvature seemed such that it could hardly be due to a multiple scattering. This tendency to curvature B. had found especially marked in the α -particles which had been deflected through large angles by atoms. The curves in this case had a tendency to orient themselves in a definite manner with regards to the initial direction of the α -particle tracks. The measurement of the curvatures of the recoil particles from 18 clear photographs of close encounters gave an av. radius of curvature of 4 mm. and this curvature was such that the particles curved away from the initial direction of the particles before encounter. An explanation suggested is that since, as Rutherford has recently shown, the α -particle has an av. charge between 0 and 1 positive units in the last mm. of its path, the asymmetry of the path may be caused by the revolution of the electron about the nucleus. Assuming that the 1 electron has an orbit of 2.7×10^{-9} cm. diameter and a velocity of 4.4×10^8 cm./sec. it will describe a trochoidal path in space as the α -particle progresses. Thus most of its time will be spent on 1 side of the α -particle. This would naturally introduce an asymmetry in the ionizing power of the α -particle on the 2 sides of its path. If it be assumed that all the ionization produced by the particle took place on 1 side of the path, the orbit would have a radius of curvature of 0.5 mm. Thus the curvature observed is easily explained by this assumption. B. then briefly shows how it is that the electron would have a preference for a rotation in such a sense that the path would be curved as observed exactly. L. B. LOEB

Chemical action of the penetrating radium rays. XV. The relation of this action to the adsorbed portion of the rays; reduction of potassium persulfate. ANTON KAILAN. *Monatsh.* 44, 35-47 (1923); cf. *C. A.* 16, 2806.—The decompn. of H_2O_2 in acid, neutral or alk. soln. and of KI in acid soln. has been measured in flasks of different forms and sizes with different "ray filters." The earlier supposition that the action of the penetrating β - and γ -rays is dependent upon the portion adsorbed is confirmed, as is also the view that of the rays taking part in the chem. action, the γ -rays form a considerable part. With the same shape of vessel, increasing the reaction space fourfold causes a relative increase in the action of 30-40%, owing to secondary effects. There is no increase in the velocity of decompn. of H_2O_2 by Ra rays when a 0.1 N Na_2CO_3 soln. is substituted for a neutral soln. In the reduction of $K_2S_2O_8$ by Ra rays the no. of reduced mols. is of the same order as the ion pairs produced by the adsorbed rays. C. J. WESS

The absorption and effective range of the β -rays from radium E. MISS A. V. DOUGLAS. *Trans. Roy. Soc. Canada* 16, III, 113-24 (1922).—When β -rays impinge on matter, *e. g.*, a metal plate, secondary γ -rays are produced, some of the β -rays are absorbed, some are scattered and some are transmitted if the plate be not too thick. If the γ -rays are due to scattered β -rays then the latter should show a loss of energy comparable with the energy of the γ -rays. Expts. are made to det. if β -rays lose velocity when scattered through large angles. A prepn. of Ra E was enclosed in a small lead case with one open face and was mounted centrally in front of, but turned away from, the foil face of an electroscope. Radiators of Pb or Ag stood in front of the active material while the absorbing material (sheets of paper) was placed behind. Only rays scattered through approx. 160° to 180° could enter the electroscope. Comparison of the intensity and percentage transmission of primary and scattered rays indicates that the scattered rays have a range only slightly less than that of the primary rays since it is certain that practically no primary rays go beyond 50 sheets of paper, while in the case of the secondary rays it is certain that some do pass 50 sheets. Other considerations

lead to the conclusion that the loss of energy is much less than 10%, and is possibly zero—a point of considerable importance since it indicates that the phenomenon of the scattering of β -rays does not furnish an explanation of the production or excitation of γ - or X-rays. The effective range of the β -rays from Ra E was detd. for C, Al, Cu, Sn, Pb and mixed foil and evidence is given to support the statement that whereas the effective range (perpendicular distance) decreases with increase in at. number, the actual range (summation distance) increases with increase in at. number. W. F. MEGGERS

Primary and secondary β -rays. J. A. GRAY. *Trans. Roy. Soc. Canada* 16, III, 125-8(1922).—Expts. similar to those performed by A. V. Douglas (cf. preceding abstr.) have been carried out with the secondary β -rays excited in Pb by X-rays which had been formed by the primary β -rays of Ra E in another piece of Pb. The results show that a large percentage of the secondary β -rays have slower velocities than the primary β -rays, thus proving that secondary β -rays, at least after their ejection from the parent atoms, can play very little part in the production of the secondary X-rays which are always formed in any substance struck by a beam of primary X-rays. W. F. M.

The mass spectrum of copper. F. W. ASTON. *Nature* 112, 162(1923).—By using CuCl in the anode ray method, A. finds 2 lines which give conclusive evidence that Cu has 2 isotopes of at. wts. 63 and 65; the intensity ratio, about 2.5:1, agrees with the at. wt. 65.37. A. suggests that Dempster's report of the 3 isotopes 62, 64, and 66 (*C. A.* 17, 3131), which is in disagreement with all other experience on the odd-numbered elements, was due to Zn impurity. R. S. MULLIKEN

A critical search for a heavier constituent of the atmosphere by means of the mass-spectrograph. F. W. ASTON. *Proc. Roy. Soc. (London)* 103A, 462 9(1923).—A crit. search for a gaseous inert element heavier than Xe was made, in which the residue absorbed in charcoal from over 400 tons of air were dealt with. The final analysis was made by means of the mass-spectrograph. The result was negative, and indicates that such an element certainly does not exist to the extent of 1 part in 10^{10} of air by vol. and probably not to the extent of 1 in 2×10^6 . Two new Xe isotopes, 124 and 126, were discovered; their percentage is extremely small. A faint band observed in the region corresponding to the mass 150 (also observed previously) was found, and is shown to be due to Hg₂⁺⁺. Another faint band was also found near 260, but no conclusion could be reached as to its origin. The results on these two bands are not in accordance with the presence of mol. Kr and Xe in the air, recently suggested by J. J. Thomson, who observed bands in the same positions. R. S. MULLIKEN

Ionization produced by the hydration of quinine sulfate. MILLE CHAMIR. *Compt. rend.* 177, 181-4(1923); cf. *C. A.* 17, 1585.—C. has made the following further observations: (1) the amt. of H₂O of hydration of quinine sulfate is 4.81%; (2) the duration of the phenomenon of hydration whether observed by increase in wt. or diminution of current is proportional to the surface density; (3) the curves of diminution of ionization current are symmetrical with the curves of increase in wt.; (4) for different wts. of salt but of the same density, the intensities maxima are proportional to the wt.; (5) the quantities of electricity liberated during hydration of quinine sulfate are proportional to the wt. of salt employed and accord with the calcd. values. L. T. FAIRHALL

An experiment demonstrating corpuscular rays. W. J. DE HAAS. *Physica* 2, 73-6(1922).—The expt. is based on Geiger's method of point discharge. The variations of potential, due to the radiation, are intensified by means of vacuum tubes, so as to allow the observation by means of a telephone. R. BEUTNER

The photoelectric velocity distribution. OTTO KLEMPERER. *Z. Physik* 16, 280-99(1923).—The electrode, which was illuminated by a Hg arc lamp, was of Zn. The enclosing app. was of brass and was divided into 4 compartments so that both methods of velocity measurement could be detd. in the same tube. Millikan's method (*C. A.* 16, 717) of opposing a counter elec. force gave, for a relatively small no. of electrons, a sharply defined max. velocity, in accord with the demands of the quantum theory, rather than an asymptotic course. A sepn. of different velocities by magnetic control, as devised by Ramsauer (*Ann. Physik* 45, 961, 1122(1914)), could be made to yield closer evidence of the same max. than was obtained by him, but the influence of electron reflection was still too strong to allow conclusions to be drawn. If the surface of the electrode was not fresh, the no. of electrons with smaller velocities decreased more rapidly than those with greater. G. R. FONDA

The use of a high vacuum hot cathode tube, working with secondary radiation, as source of oscillations. K. W. HAUSSER. *Wiss. Veröff. Siemens-Konzern* 1, 19-23 (1920); *Physik. Ber.* 3, 1326.—A. W. Hull has devised a set-up with a hot cathode tube which, by using secondary rays, is suitable for producing oscillations. This arrangement is discussed and its efficiency calcd. Conclusion: It is useful only for low power

and then only when one succeeds in obtaining a large no. of secondary electrons for one primary.

Haidinger's polarization brush effect. PAUL LIESEGANG. *Central-Zig. Opt. Mech.* **43**, 355-9(1922); *Physik. Ber.* **3**, 1179.—This can be seen by a large audience when a Liesegang analyzing screen on which polarized light falls is employed. Because of its great brightness an Al screen is preferred. A blue disc is advantageously inserted which renders the blue brush black and contrasting. The intensity decreases with time and the direction of polarization must be changed. An explanation of the phenomenon is given.

Disturbed electron orbits in an electromagnetic field. PANCHANAN DAS. *Bull. Calcutta Math. Soc.* **12**, 203-8(1922); *Physik. Ber.* **3**, 1117.—A plane polarized wave is directed onto a H-like atom in which the valence electron is describing a circular orbit. D. neglects, as usual, the magnetic effect of the light wave, and considers 2 special cases. He explains a decrease in width of lines with rising temp. by at. collisions where specified quanta exchanges between the disturbed orbits of the valence electrons take place. The occurrence of resonance radiation is discussed.

Rotation of electric discharge in a magnetic field and the determination of molecular diameters. C. E. GUYE AND R. RUDY. *Arch. sci. phys. nat.* **5**, 182-96(1923).—See *C. A.* **16**, 2807.

The scattering of electron by a positive nucleus of limited field. C. DAVISSON. *Phys. Rev.* **21**, 637-49(1923).—In order to apply to the scattering of β -particles and electrons by the nucleus of the atoms the type of considerations used by Rutherford for α -particles D. points out that the theory must take account of the shielding action of the other electrons in the atom. For owing to the small energy of the electrons they are scattered appreciably at far greater distances from the nucleus than are the α -particles. As a rough approximation to such a treatment he assumes that the inverse square law holds for electrons that lie within a certain distance r from the nucleus. Beyond this distance he assumes that owing to the action of the at. electrons, the force causing scattering of electrons or β -rays is 0. This assumption serves as a basis for the mathematical treatment of the scattering, and by means of semi-graphical methods he is able to det. the scattering to be expected. The comparison of the consequences of this theory with the actual exptl. results on scattering will be published shortly.

Electron emission from metals as a function of the temperature. SAUL DUSHMAN. *Phys. Rev.* **21**, 623-36(1923).—Considering the evapn. of electrons from metals equiv. to the evapn. of a monat. gas D. derives an expression for the electron emission from metals as a function of temp., on the basis of the Nernst heat theorem. If the sp. heat of the electrons in the metals is 0 while in a free state the sp. heat of the electrons is the same as that of a monat. gas the equation obtained is $I = AT^2 e^{-b_0/T}$, where $b_0 = \phi_0/k$ and $\phi_0 = \phi - 1.5 kT$, ϕ being the Richardson thermionic work function, k the Boltzmann const., and e the electron. An equation of this form has been suggested before but has not been derived from this point of view. The importance of this equation lies in the fact that the const. A is theoretically a universal const. From the Sakur-Tetrode equation for the chem. const. i_0 , A becomes 60.2 amp. per cm. per deg.², while the theory of rational units of Lewis gives 50.2 amp. per cm.² per deg.². Recent results of Davisson, Germer, and Schlichter, as well as some of D.'s own results agree as well or better with the new equation than with the old one. Owing to the uncertainties of temp. measurement it is impossible to decide which value of A is correct. From the known values of b_0 he computes the work function ϕ from this theory.

Deflection of a stream of electrons by electromagnetic radiation. E. O. HULBURT. *Phys. Rev.* **21**, 650-2(1923).—H. derives the mathematical theory of the deflection of a stream of electrons by electromagnetic radiation on the basis of the classical laws of electrodynamics. When certain approximations are made he obtains a max. angle of deflection given by $He/m\omega$, where $\omega/2\pi$ is the frequency of the radiation and H is the field due to it. For sunlight H is 0.04 and the corresponding value of the deflection is 4×10^{-16} , while for intense X-rays it is 10^{-12} . These deflections are too small to detect exptly. Thus if some recent expts. by C. J. Lapp, which indicate such an effect, prove to be correct the results will be in direct conflict with classical electrodynamics.

Exercises in electronic theory. I. Delayed potentials. II. Force and current of energy. A. D. FOKKER. *Physica* **1**, 129-40, 199-207(1921).—Formulas are derived for the retarded potentials in optional distance of moving elec. charges. In the second publication, these formulas are applied for detg. the distribution of energy around

an electron. Conclusion: The radiation does not always stop if the so-called resistance of radiation is lacking as most of the energy of radiation is produced from the stock of energy of the elec. field.

R. REUTNER

The conduction of electricity in gases. I. General points of view on the motion of electrons and ions in gases. II. Methods for studying the quantum change of energy in the colliding of electrons and gas molecules. G. HERTZ. *Physica* 2, 15-26, 61-73(1922).—A review.

R. REUTNER

The spark discharge. JULJA FINKELSTEIN-CUKIER. *Ann. Physik* 71, 503-36 (1923).—Photomicrographs were made showing that the characteristics of the point to plate spark discharge depend upon the microscopic condition of the electrode points. The light around the point increases with the voltage. With suitable cone-shaped electrodes, positively charged, an empirical law is followed as long as fresh air is supplied; but in stagnant air the results are not reproducible.

F. O. ANDEREGG

The high-frequency discharge in rarefied gases. C. GUTTON, S. K. MITRA AND V. YLOSTALO. *Compt. rend.* 176, 1871-4(1923). With a sine wave current at frequencies varying from 50 to 2×10^6 the discharge started at higher pressures the higher the frequency with interior electrodes. In the electrodeless discharge at 0.5-1.5 mm. of air an optimum frequency for ease in starting the discharge was observed which varied with the tube.

F. O. ANDEREGG

Some characteristics of electron tubes. II. GREINACHER. *Z. Physik* 11, 503-52 (1923).—The validity of the $3/2$ law for cylindrical electrode tubes was confirmed provided that the working voltage is taken as the algebraic sum of the applied and heating voltages, the emission energy and contact potentials. Detn. of the consts. of the $3/2$ law indicates that the usual Langmuir-Barkhausen expression should be replaced by another. Some expts. are described on the magnetic effect of a stream of electrons by means of which a new e/m detn. may be made. A strong magnetic field may cause the electrons to return completely to the hot wire.

F. O. ANDEREGG

Disruptive potentials in gases at elevated pressures and the molecular field. III. C. E. GUYE AND J. J. WEIGLE. *Arch. sci. phys. nat.* 5, 196-207(1923); cf. C. A. 17, 2386, 2992.—When a dipole is agitated thermally although not in any external elec. field, a polarization is produced through collision which aids the passage of a disruptive discharge. This is especially marked with the more polar gases, those which deviate most from the gas laws. Thus CO_2 fails to follow Paschen's law while the much less polar N follows it closely, just as it is less imperfect.

F. O. ANDEREGG

Regularities in the anomalous Zeeman effect. W. PAULI, JR. *Z. Physik* 16, 155-64(1923).—From the observed resolution of spectral lines in the anomalous Zeeman effect Landé and Sommerfeld detd. the resolution of the combination terms in the doublet spectra of the alkalis and the triplet spectra of the alk. earths. Recently Landé (C. A. 17, 2992) in a similar quantum-theoretical analysis generalized the previous results for an extensive class of multiplets in a weak outer magnetic field. In the present paper, values of the combination terms for Landé's multiplets in strong outer magnetic fields are given in formal rules governing certain quantum numbers m , k , which det. the Zeeman resolution factor g . A rule that the sum of energy values in all those stationary states which belong to given values of m and k remains, during the transition from weak to strong fields, a linear function of the field strength permits calcn. of the g -values when the term values for strong fields are known. A satisfactory mech. explanation of these Zeeman regularities on the basis of the known principles of the quantum theory seems impossible at present.

W. F. MEGGERS

A new secondary radiation of X-rays. W. BOYDE. *Z. Physik* 16, 319-20(1923).—Photographs of a pencil of hard X-rays in air and H_2 , made by the Wilson fog method, show the presence of fog-forming nuclei within the pencil. The tracks are short and differ from electron tracks in that they leave off sharply at both ends. Distinct tracks were not obtained in H_2 with soft X-rays.

J. A. ALMQUIST

Penetration of Röntgen rays into homogeneous and non-homogeneous substances. H. WINTZ AND W. RUMP. *Fortschr. Geb. Röntgenstr.* 29, 580-6(1922); *Physik. Ber.* 3, 1169.—The ionometric observation that the intensity of Röntgen radiation diminishes with increasing depth of water layer traversed is not in accord with the photographic measurements of Dessauer and Vierheller. For the latter, after a certain depth, a nearly const. value was obtained. The distribution of intensity sideways from the central beam into the water, and the influence of the air space on the depth change are to be investigated.

A. E. STERN

Physical properties and biological effects of Röntgen radiation from the rear of the anticathode. L. HALBERSTÄDTER. *Fortschr. Geb. Röntgenstr.* 29, 478-88(1922); *Physik. Ber.* 3, 1159.—With the aid of photographs and intensity measurements (electro-

scopic, photographic, and with Se cell) it is shown that, apart from the secondary radiation of glass walls, (1) for gas-contg. Röntgen tubes, only the face of the anticathode emits Röntgen rays, (2) for gas-free tubes (Coolidge or Lilienfeld tubes) the back of the anticathode also emits these rays, and that in the Coolidge tube, at about 180,000 v., this 'back face' radiation is about $1/2$ the intensity of the radiation from the front. By electroscopic absorption measurements and measurements with an analyzer, H. showed that radiation from the back face is softer. He makes a series of recommendations regarding protection of patient and operator in using these tubes. A. E. STEARN

A new form of the Rubens residual ray method. MARIANUS CZERNY. *Z. Physik* 16, 321-31(1923).—A method is described for the production of residual rays which requires only a single reflecting surface, the other wave lengths being removed by the use of polarizers. Expts. with CaF_2 , KCl , KBr , KI and NaCl indicate that the purity of the residual rays obtained in this way is comparable to that given by the old method with 3 to 5 reflecting surfaces. J. A. ALMQUIST

Combination relations and terms in the band spectrum of helium. A. KRATZER. *Z. Physik* 16, 353-66(1923); cf. *C. A.* 16, 2077; 17, 1588.—Combination relations are found for the He bands, 6400, 4546 and 5730 Å. The moment of inertia of the He mol. is calcd. to be 0.944×10^{-40} g. cm.² J. A. ALMQUIST

Spectra produced in electrode-free ring currents. HANNS JUNG. *Verh. Phys. Ges.* 3, 6-7(1922); *Physik. Ber.* 3, 786-7.—Short notice of a lecture the details of which are published elsewhere. Hg or Na vapor was distd. under high vacuum into bulbs and sealed off, and the requisite vapor pressure obtained by heating. For Hg the spectrum was pure. At 0.07 mm. it showed the known spectrum, triplets, single and combination lines as well as spark lines. At 0.45, 2.7 and 8.5 mm. only a few lines appeared. They were weaker and the spark lines were about gone. A continuous band from 6000 to 3500 Å. appeared with increasing vapor pressure. The Na bulb showed at low vapor pressure (200-300°) the series spectrum. The K, present as impurity, gave at 200° intensive series and spark lines, which were about gone at 225°. Above 325° the glass absorbed all the alk. metal. The results are in accord with Bohr's theory. The cond. curve for Hg vapor corresponds exactly to that described by Wachsmuth for gases, that of Na less so. A. E. STEARN

Characteristics of selenium cells exposed to light. A. WENDT. *Verh. Phys. Ges.* 3, 26(1922); *Physik. Ber.* 3, 789.—The stream-intensity curves for cells with small 'dark' effect show upon exposure pronounced satn. characteristics. In the first straight line portion of the curves the light stream is proportional to the sq. root of the exposure intensity. Farther on it increases more rapidly. A. E. STEARN

Dependence of the photostream on the temperature of the light source. K. BERGWITZ. *Verh. Phys. Ges.* 3, 25-6(1922); *Physik. Ber.* 3, 788.—The statement that the relation between the thermal electronic emission from an incandescent metal and its temp. is the same as that between the emission of a metal electrically lighted and the temp. of the light source is confirmed with the help of Pt vessels heated in an elec. oven and of a high sensitivity K-cell. A. E. STEARN

The ruled grating in spectroscopy. A. LO SURDO. *Atti. accad. Lincei* 30, I, 136-9 (1921); *Physik. Ber.* 3, 859-60.—A theory of the ruled grating is developed in which the difference in path is not produced, as in the Michelson grating, by different thicknesses of glass layer passed through, but by reflection from the face of the lines. If t is plate thickness, s is width of rulings and N is total no. of rulings, then for

$$\begin{array}{lcl} \text{Dispersion} & d\theta/d\lambda = -2t/\lambda S & [t/\lambda S((n-1) - \lambda dn/d\lambda)] \\ \text{Analysis} & d\lambda/\lambda = \lambda/2tN & [\lambda/tN((n-1) - \lambda dn/d\lambda)] \\ \text{Angle width of} & & \\ \text{1st order} & d\theta = -\lambda/S & [\lambda/S] \end{array}$$

The formulas in parentheses are the corresponding ones for the Michelson grating. The dispersion and resolution are seen to be 3 times as great and the range of wave length about $1/2$ that of the Michelson grating. Michelson, who first thought of using the catoptric type, changed to dioptric because the former required much finer adjustment. Improvement in technic now makes possible the latter. S. succeeded in resolving the Hg line 5770 perfectly into its components with a small Hülger grating used catoptrically, an expt. which required a much larger grating the other way. A. E. STEARN

A simple method for measurement of absorption in the ultra-violet. H. CHR. WINTHER. *Z. wiss. Phot.* 22, 125-30(1923); cf. *C. A.* 17, 1587.—Photographic exposures were first made through an oxidized Cu gauze, which reduced the intensity a fixed amt., independent of the wave length, and then, on adjacent strips of film, through various thicknesses of soln. The absorption was found by selecting points of equal exposure. G. R. FONDA

The quantum theory of line spectra. III. NILS BOHR. *Mem. acad. roy. sci. lettres Danemark* 4, No. 1.—This paper constitutes a very tardy publication of the third section of a series of 3 papers by B. on Quantum Theory (*C. A.* 17, 1374). It deals with spectra of elements of higher at. no. B. states that owing to certain unsatisfactory points in the theory, and to the rapid advance of the subject, the publication of this section had been withheld for 4 years. This paper consists of original manuscript as it was written in 1918, with B.'s comments, in view of the recent advances. It was published chiefly with a view to completing the series of 3 papers rather than because it contained any new views.

The doublet separations of Balmer lines. J. C. McLENNAN. *Nature* 112, 106 (1923).—New work by G. M. Shrum leads to excellent agreement with Sommerfeld's predicted value, 0.36 cm.^{-1} , for the doublet sepn's. of the Balmer lines. By the use of special tubes cooled with liquid air, observations were made on H_{α} , H_{β} , H_{γ} , H_{δ} , and H_{ϵ} . The observed sepn's. were, resp., 0.33 ± 0.02 , 0.36 ± 0.01 , 0.37 ± 0.02 , 0.36 ± 0.02 , and 0.35 ± 0.02 . Cf. *C. A.* 16, 684.

Absorption spectra of pyrrole and of its derivatives. I. The absorption spectrum of pyrrole. T. V. KORSHUN AND K. V. ROLLA. *J. Russ. Phys. Chem. Soc.* 49, I, 153-8 (1917).—In opposition to the findings of Hartley and Dobbie (*J. Chem. Soc.* 73, 603 (1897)) and of Purvis (*C. A.* 4, 3213), K. and R. found by using more concd. alc. solns. of pyrrole and its derivs. that they possess definite absorption spectra. Alc. solns. of pure pyrrole in 2*N*, 0.1 *N* and 0.01 *N* concns. show 2 absorption bands, the 1st band within the range of $1/\mu$ —3200-3500 and the 2nd in the vicinity of $1/\mu$ —3750. The derivs. of pyrrole give absorption spectra approx. within the same ranges but of much greater intensity as shown by the depths of the layers of the derivs. being 200-1000 times less than those of pyrrole. It is pointed out that these findings are an alioquo to those of N. A. Valiashko who showed (*J. Russ. Chem. Soc.* 46, 1820-2 (1914)) that the Ph nucleus plays the detg. role in the position of the spectra of its derivs. W. A. PERLZWEIG

Disturbances and the principle of combination in the system of the violet cyanogen bands. A. KRATZER. *Munch. Ber.* 1922, 107-18; *Physik. Ber.* 3, 1080-1.—From the distribution of the disturbances in the system of the violet cyanogen bands it is concluded that these may be ascribed to disturbances of the initial term. This is not in agreement with Heurlinger's representation of the partial bands; rather must the numbering be so changed that for all the lines the current no. is decreased by 0.5. The violet bands consist of partial bands which can be represented approx. by the formula $\nu = A + 2Bm + Cm^2$, where *m* can take all values of half integers. This numbering is further supported by the fact that only thus is the principle of combination between the partial bands of the system satisfied. Theoretically this result is regarded to mean that in the calcn. of mol. energy the mutual effect of electron motion and the motion of the mol. as a whole is considered. This energy is not an even multiple of $h^2/8\pi^2J$, and so gives rise to a fractional current no. Cf. *C. A.* 16, 682, 2638. A. E. STEARN

Regularities in the arc spectrum of vanadium. W. F. MEGGERS. *J. Wash. Acad. Sci.* 13, 317-25 (1923).—The displacement law of Kossel and Sommerfeld led to the alternation law which states that the even and odd structures of both arc and spark spectra alternate between adjacent columns of the periodic classification. This law originally was verified only for the first 3 columns, but recent work on Ti, Cr and Mo, Mn, and Fe established its validity for arc spectra for columns IV, VI, VII, and VIII. In the arc spectrum of V regularities have been found which verify the law for column V also. These regularities, called multiplets, are groups of lines of the same temp. class linked together by recurring const. wave-no. differences. In all, 16 such groups are presented, in one of which the *raies ultimes* are included. C. C. KIESS

The influence of an electric field on the series spectrum of helium. W. TSCHULANOWSKY. *Z. Physik* 16, 300-13 (1923).—Under normal conditions of excitation, in which no external elec. field is present, the spectrum of He consists of singlet and doublet series between which no combinations occur. However, in the presence of an elec. field appear new lines, some of which have been identified as the prohibited combinations $2P - mP$, $2S - mS$, $2S - mD$, for the singlet series, and similar combinations for the doublet series. Since the terms *mS*, *mP*, and *mD* are known the combination series $2P - mD$ is readily calcd. Among the hitherto unidentified lines, brought out in an elec. field, are the combination series with the Bergmann and ultra-Bergmann terms, such as $2P - m\Delta$, $2P - m\Delta^{(1)}$, etc. It is shown that the terms $m\Delta$, $m\Delta^{(1)}$, $m\Delta^{(2)}$, etc., although unknown, are smaller than *mD* but differ from them by less than certain small amts. It is thus possible to locate the lines of the series $2P - m\Delta$, etc., close to and on the violet side of the lines of the series $2P - mD$, which will thus appear to have a "fine structure." The observations of Stark, of Koch, and of Liebert on both

the singlet and doublet series furnish data which confirm the scheme just outlined. T.'s measurements of Paschen's spectrograms of He permit the detn. of $m\Delta$ for 4 lines in the singlet series $2P - m\Delta$, and for two lines in the doublet series. C. C. KIESS

Röntgen spectroscopy of metal compounds. KARL BECKER AND FRITZ EBERT. *Z. Physik* 16, 165-9(1923).—Although the space-gratings of most metals are known, practically no Röntgen spectrographic studies of metal compds. have been made. Results by the method of Debye and Scherrer have now been obtained for a no. of metal compds., viz., $\text{Cu}_2\text{Zn}_3 + 96.3\%$ wt. $\text{Mg}_2\text{Al}_3 + 3.7\%$ wt. Al, NiAl, CuAl, Cu₂Al, Ni₂W and W-Ni with 6% Ni. The first 3 possess regular gratings and for these quant. data on the edge of the elementary cube, its vol., the no. of mols. or atoms contained, the mol. wt. and the computed d. are given. W. F. MEGGERS

The electrodeless discharge in iodine and in hydrogen. J. K. ROBERTSON. *Trans. Roy. Soc. Canada* 16, III, 151-5(1922).—Results of a spectroscopic study of the discharge excited in certain vapors by electromagnetic induction have been given in another paper (cf. C. A. 16, 2450). The investigation has been extended to other diatomic gases and vapors, especially to H_2 , and a qual. description of spectral changes occurring with variations in the gas pressure and length of spark gap is presented. W. F. MEGGERS

Photochemistry and electrochemistry. J. LIFSCHITZ. *Chem. Weekblad* 19, 21-6(1922).—L. discusses the theoretical causes of the *Hallwachs effect*—negative charge acquired by a metallic plate under radiation—and of the *Bequerel effect*—galvanic current produced by radiating 1 of 2 electrodes. As shown by E. Baur a current is produced, also, if the electrolyte only is radiated. The Hallwachs effect is due to an expulsion of electrons from the sphere of action of the at. nucleus while, in the Bequerel effect, some electrons are thrown into another orbit by the action of the light. The Bequerel effect is, therefore, not exactly a Hallwachs effect of the electrolyte; it is, however, the electrochem. consequence of the primary photochem. process, produced by radiation. R. BEUTNER

Electron theory of valency applied to coördination compounds (SPIERS) 6. The electronic theory of valency. II. Intramolecular ionization in organic compounds (LOWRY) 2. Possible error in the theory of coördination (LOWRY) 6. Chemical formula of uraninite (SCHÖPF) 8. A general and uniform application of the quantum theory, and a quantum theory of dispersion (SMEKAL) 2. Electrochemistry of gases (LIND) 4.

ANDRADE, E. N. DA C.: **The Structure of the Atom.** London: Bell & Sons, Ltd., York House, Portugal St., W. C. 2. 314 pp. 16s. net. Reviewed in *Chem. News* 127, 142(1923).

BLAIR, E. W., AND WHEELER, T. S.: **The Constitution of Matter.** London: Methuen & Co., Limited. 6s net. Reviewed in *Engineering* 116, 141(1923).

DAMIENS, A.: **Isotopes.** Paris: Gauthier-Villars & Co. 118 pp. F 12.

GERLACH, W.: **Materie, Elektrizität, Energie: Die Entwicklung der Atomistik in den Letzten Zehn Jahren.** Vol. VII. Wissenschaftliche Forschungsberichte. Naturwissenschaftliche Reihe. Edited by Dr. R. E. Liesegang. Dresden and Leipzig: T. Steinkopff. 195 pp. 3s. 3d.

KAYE, G. W. C.: **X-rays.** 4th Ed. Revised. London and New York: Longmans, Green & Co. 320 pp. \$5. Reviewed in *Proc. Am. Soc. Civil Eng.* 49, 439 (1923).

4—ELECTROCHEMISTRY

COLIN G. FINK

Hertha Ayrton. ANON. *Electrician* 91, 227; *Elec. World* 82, 509(1923).—Obituary. C. G. F.

Electrochemistry and electrometallurgy in Switzerland. ANON. *J. four élec.* 32, 107-9(1923).—A review covering the years 1914 to 1922. C. G. F.

Progress in the manufacture of steel in the electric furnace. CLAUDEL DE COUSSENGES. *Rév. métal.* 20, 417-22(1923).—Discussion of the advantages of the elec. furnace with a description of the various types and their merits and disadvantages.

Progress in the electrometallurgy of zinc. A. BILLAZ. *Technique moderne* 15, 481-90(1923).—A review. A. PAPINEAU-COUTURE

Eddy currents in iron masses. E. ROSENBERG. *Electrician* **91**, 188-91(1923).—A development of a formula for the treatment of eddy currents in Fe masses using the simplest phys. assumptions. The formula is $P = 2 \times 10^{-4} \sqrt{\rho N^2 f}$, where P = eddy loss at the surface, watts per cm.², ρ = resistivity, f = frequency and N = amp. turn per cm. (r.m.s. value). Exptl. data are given as confirmation of the formula.

W. E. RIDGER

The manufacture and use of amorphous carbon and of graphite electrodes. FRANÇOIS GALL. *Rév. métal.* **20**, 452-6(1923).—A description of the qualities of amorphous C and graphite as electrode materials, of their manuf. and uses.

A. P. C.

Relation between current, voltage, and the length of carbon arcs. H. A. E. R. WESTMAN AND W. J. CLAPSON. *Trans. Am. Electrochem. Soc.* **44**, (preprint); cf. *C. A.* **17**, 1756.—Conditions have been found under which steady arcs can be maintained with currents from 120 to 700 amps. and voltages from 15 to 60 v. The voltage over the arc = 0.99 times the length in mm. from the tip of the cathode to the bottom of the anode crater.

D. MACRAE

Repulsion effect between the poles of an electric arc. H. M. BARLOW. *Phil. Mag.* [6] **46**, 112-4(1923).—A note suggesting a new repulsive force between the pole of an arc, either with a.c. or d.c. The "pinch" effect which is a tendency for the lines of current flow to constrict themselves toward the axis would result in a lengthening along the axis, and consequently a repulsive force on the poles. It is calculated that for a 20 amp. current this force would account for 30% of the observed repulsion.

S. C. LIND

Induction furnaces for non-ferrous metals. EMILE DEMENGE. *Rév. métal.* **20**, 148-52(1923).—After a brief outline of the merits of induction furnaces, D. describes in detail a furnace used by the Compagnie Française des Métaux which can effect continuous or variable agitation of the molten metal, allows of decanting clean metal, reduces oxidation and radiation losses to a min., and can be connected directly and simultaneously to the 3 phases of an ordinary circuit with an acceptable load factor.

Also in *J. four. élec.* **32**, 53-5(1923).

A. PAPINEAU-COUTURE

The future of the world's aluminium industry. ROBERT PITAVAT. *J. four. élec.* **32**, 100(1923).

C. G. F.

Note on the production of silicon-aluminium alloys. F. D. *J. four. élec.* **32**, 102(1923).

C. G. F.

Electrolytic metallurgy of non-ferrous metals. ALTMAYER. *Rév. métal.* **20**, 438-41(1923).—Brief description of recent progress in the electrolytic metallurgy of Cu, Zn, Cd, Sn, Ni and precious metals.

A. PAPINEAU-COUTURE

The preparation of potassium chlorate by the electrolysis of sodium chloride. E. V. ALEKSEEVSKII. *J. Russ. Phys. Chem. Soc.* **53**, 1, 323-5(1921).—The electrolysis was conducted in a beaker using Leclanché carbon elements as electrodes and KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ as depolarizer. To 140 g. NaCl and 1 g. of the depolarizer dissolved in 500 cc. H_2O 36 g. K_2CO_3 were gradually added. With a current density of 5 amperes per sq. dm. of electrode and an e.m.f. of 8 v., 64 amp. hrs. were used. The distance between the electrodes was 1 cm. After filtering off the suspended C, evapn., and drying at 110°, 115 g. residue were obtained contg. 42.3 g. KClO_3 equiv. to a 91.8% current efficiency.

W. A. PERLZWEIG

The solubility of potassium chlorate in aqueous solutions of sodium carbonate, of sodium chloride and of potassium carbonate. E. V. ALEKSEEVSKII. *J. Russ. Phys. Chem. Soc.* **53**, 1, 326-31(1921).—The results given in the table below were obtained in an effort to devise a method of recovering the KClO_3 from the electrolysis mixt. (cf. preceding abstr.). The detns. were made in const. temp. water baths, a max. time of 3 hrs. being allowed for the soln. of each added portion of 0.1 g. The values are in g. per 100 cc. solvent.

Temp.	5 & 7% Na_2CO_3	5% NaCl	30% NaCl	5%	10%	20%	30%	40%	50%
				K_2CO_3					
20°	5	5	5	6	5	4	2.5	2	1
30	5.5	5.5	5.5	6.5	6	5	3.5	2.5	2.5
40	7.5	7.5	6.5	8.5	8	6.5	4.5	4.5	3.5
50	10.5	13	11.5	9.5	9	7.5	6	6	4

From these data A. concludes that it is possible to recover the KClO_3 from the electrolysis mixt. by evapg. the soln. to $1/2$ vol., crystg. at 20°, removing the cryst. crop and repeating this process once with the supernatant liquid. The remaining mother liquor may be dild. to the original vol. of 500 cc. and réemployed for the electrolysis. W. A. P.

Electrical discharge through gases. R. SEELIGER. *Siemens Z.* 3, 14-9, 280-6, 302-8(1923).—A review. C. G. F.

Electrochemistry of gases. S. C. LIND. *Trans. Am. Electrochem. Soc.* 44, (preprint)(1923).—Gas ions tend to form addn. products with neutral mols., which complexes are the intermediate products of gaseous electrochem. reactions. It follows that ions do not interact nor do mols. or atoms otherwise activated interact. Their momentary concns. are too low. They react only with neutral or unactivated mols. A low momentary concn. of activated substance is capable of explaining the action of negative catalysts or inhibitors. Active ions may be destroyed by reverse action either in a uni- or multi-component system, without any effective chem. action resulting. The reversal may be prevented by a suitable acceptor. Free electrons will play a primary part in producing chem. reaction only in gaseous systems contg. at least one gas with affinity for electrons. A secondary role is always played by electrons in restoring final elec. neutrality. The above general principles are illus. by instances of the behavior of CO, CO₂, CO + H₂, CO₂ + H₂, and O₂ + H₂ under the influence of α -radiation. D. MACRAE

Chemical action and the disappearance of gas in the electrical discharge tube. F. H. NEWMAN. *Trans. Am. Electrochem. Soc.* 44, (preprint)(1923).—H and Na are absorbed in the presence of different elements, deposited on the cathode of a discharge tube, when the discharge is passing. The elements which show this effect most markedly are P, S, I, Na, K, and the alloys of Na and K. The rate of disappearance is greatest with P, S, and I, and the final pressure attained is a min. with P and S. There is similar absorption when the gases are ionized by α -rays from polonium. The disappearance of the gas is due to the production of chem. compds. The formation in this manner of the nitrides of Na, K, Mg, and Sn, and of the hydrides of Na, K and S have been proved by chem. analysis. The gas under the ionizing effect becomes modified, assuming an active condition which consists probably of triatomic mols. D. MACRAE

Thermionic valves on public supply systems. P. D. LOWELL. *Electrician* 91, 147(1923); 4 illus. C. G. F.

Relative air density in high-voltage testing. E. D. DOYLE. *Elec. World* 82, 329(1923). C. G. F.

Notes on the operation of the mercury arc rectifier. A. ROTHENBERGER. *Siemens Z.* 3, 234-8(1923). C. G. F.

Recent measurements of dielectric losses. H. ZICKNER. *Elektrotechn. Z.* 44, 762(1923).—A brief discussion and comparison of the method of measurement employed by Schott, Steinhaus and Geyger, to det. the dielec. losses in various materials, glass, mica, hard rubber, etc., such as are used in condensers and other high frequency app. W. E. RUDER

The measurement of power losses in dielectrics. L. HARTSHORN. *Beams* 13, 89-99(1923).—A discussion of the bridge methods used for this purpose by Schering, Monasch, Wagner, Semm, and others. The Schering bridge is considered most useful for practical measurements. Diagrams of the various bridge connections are given. In using this method particular attention must be given to capacities and leakages of the arms to earth, stray capacities and mutual inductances between various arms of the bridge, inductive effects between the source of current and the detector, and to phase angles of resistances and condensers. W. E. RUDER

Filling materials for high current cable fittings and their chemical composition. J. W. UYTENBOGAART. *Elektrotechn. Z.* 44, 706-8(1923).—A discussion of the influence of free C, SiO₂, Al₂O₃, CaO, org. acids, and moisture in the various fillers and binders used. W. E. RUDER

Receiving microphones or thermophones. LESLIE MILLER. *Electrician* 91, 146(1923). C. G. F.

Vitreous enameling in the electric furnace (YARDLEY) 19. Sealing base metals through glass (HOUSEKEEPER) 1.

STRICKER, KARL: *Jahrbuch der Elektrotechnik*, 1921. München: R. Oldenbourg. 237 pp. \$1.00. Reviewed in *Proc. Am. Soc. Civil Eng.* 49, 443(1923).

Galvanic batteries. K. KAWAKAMI. *Brit.* 193,087, Oct. 13, 1921. A porous alloy of Pb, Sb and Hg for use in storage battery electrodes is made by subjecting a heated alloy of the 3 metals to treatment in a centrifugal separator whereby an eutectic alloy is driven off leaving the remaining alloy in a porous condition.

Electric heating element. E. A. A. GROENWALL. Swed. 52,640, Sept. 6, 1922. The element consists of a plate, cylinder or pole of graphite or another carbonaceous material, divided in lamella and provided with legs of the same material. It can be mounted in a furnace without touching the walls. Cf. *C. A.* 17, 1759.

Electric production of steel. I. RENNERTFELT. Swed. 51,728, July 26, 1922. Iron ore and lime and eventually other required materials are placed in the bottom of an elec. furnace and strongly heated by radiation from arcs above the charge. Then liquid pig-iron is poured over the materials and the charge is heated at first from arcs in contact with the bath and finally by freely burning arcs.

Electric refining of steel. I. RENNERTFELT. Swed. 51,415, June 14, 1922. The charge of liquid steel is at first treated with an elec. arc playing on the bath in order to promote strong circulations in the steel which facilitate the refining reactions. Finally it is heated (preferably in the same furnace) by elec. arcs independent of the charge.

Production of electrolytic iron. AVESTA JERNVERKS A.-B. Swed. 51,893, June 14, 1922. The electrolyte is a hot soln. of ferrous salts. The cathode is kept at a lower temp. than the electrolyte.

Reduction of ores. A. G. THISELL. Swed. 51,930, June 14, 1922. The ore is fused in an elec. furnace with graphite ore or other graphite-contg. materials as a reducing agent in combination with a carbonaceous material or other materials less conductive than graphite, for instance powd. charcoal.

Decomposition of alkali aluminium silicate. A. R. LINDBLAD. Swed. 51,522, Apr. 26, 1922. Feldspar, leucite or other minerals contg. alkali Al silicates are mixed with adequate amts. of lime and fused in an elec. furnace. The liberated volatile alkali compds. are drawn off, the furnace working under reduced pressure.

Ozone. OZON-HOCHFREQUENZ GES. Brit. 193,422, Feb. 17, 1923. Ozone is produced by means of currents of frequency between 1000 and 100,000, obtained from high-frequency dynamos or from frequency transformers. Large loads can be applied to the ozonizers without decrease of yield. In large app. intensive cooling of the air is necessary. To prevent destruction of the dielectric, it is thickened at the ends, or a large air-gap is provided within the field of the cooled outside coating.

Crystalline minerals. CARBORUNDUM CO. Brit. 193,081, Sept. 19, 1921. The bonding qualities of cryst. materials, e. g., abrasives, refractories such as corundum, emery, garnet, quartz, silica sand and SiC, are improved by pitting or etching the surfaces by heating the grains to a temp. of over 212° F. with 2% or less of an acid substance distributed in small particles more or less evenly over the surfaces of the grains. Example, grains of fused Al_2O_3 are moistened with a soln. of H_3PO_4 , and heated to about 500° F. for an hr. Suitable acid substances are H_3PO_4 , fluosilicic acid, H_2SO_4 , HNO_3 , chromic acid, silicic acid, or their salts. The grains are bonded by binding agents such as glue, rubber, shellac, clay, cement, etc.

5—PHOTOGRAPHY

C. E. K. MEES

Photographic progress in 1922. R. E. CROWTHER. *Brit. J. Phot.* 70, 416-49 (1923).—A reprint of the section on photography of the reports of the Soc. of Chem. Industry. Mention is made of the new photographic periodicals that have appeared and of changes in time of publication of older journals. Considerable space is devoted to a discussion of developments in cinematography with special emphasis directed to the revival in interest in home picture app. Numerous processes of color photography have appeared, one of these including the means for producing a black and white component in three-color photography. Contributions on the keeping qualities of sensitized emulsions and on the prepn. of new sensitizing dyes have appeared, notably thiocyanine and carbothiocyanine, and several new sensitizers for the deep red. The theory of desensitization and the introduction and uses of pinakryptol and pinakryptol green are discussed. Properties and characteristics of developers, observations on the chemistry of fixing baths, and methods of washing each receive attention. Persulfate reduction, the influence of colloidal S in toning, and the use of tin compds. in toning silver images are dealt with.

The applications of photography to chemistry. PIERRE JOLIBOIS. *Bull. soc. chim.* 33, 229-45 (1923).—A lecture. H. G.

Color photography. GIRAUD. *Bull. soc. ind. Rouen* 51, 67-77 (1923).—An address on the history and present status of the problem and on the new Dufay process for obtaining positives on paper, glass or films. A. PAPINEAU-COUTURE

Change of silver sulfide to red tones and the composition of the changed image. A. LUMIÈRE, L. LUMIÈRE, AND A. SEYEWETZ. *Bull. soc. franç. phot.* 10, 159-62(1923).—The change of sulfide images to reddish tones by treating the former with AuCl_3 and an org. S compd. such as $\text{CS}(\text{NH}_2)_2$, $\text{C}_6\text{H}_5\text{N}_2\text{S}$, or NH_4CNS is discussed. The toning is a sp. reaction of the Ag_2S , which adsorbs Au to about 133% of the weight of Ag and, also, an amt. of S somewhat greater than that required to form Au sulfide. The toned image, therefore, appears to consist of a double sulfide of Ag and Au. C. E. K. MEES

The preparation of safelights. P. V. NEUGEBAUER. *Phot. Rundschau* 60, 55-8 (1923).—To make the safelights, fixed-out plates were bathed in a soln. of the dye as suggested by Lumière and Seyewetz. After examg. more than 70 different Höchst dyes to det. their suitability for the prepn. of safelights, the following were chosen: No. 1 La. Tartrazine 3%, lb. Naphthol orange 2%; No. 2 Acid rhodamine 3%; No. 3 Crystal violet 1%. No. 1 is prepd. on two plates and these are bound together. No. 1 is satisfactory for chloro-bromide paper; Nos. 1 and 2, for bromide paper, chloro-bromide plates, and ordinary plates; Nos. 1, 2, and 3 for orthochromatic plates, the absorption limits being 5500 Å., 6100 Å., and 6500 Å., resp. Panchromatic plates of slight red sensitiveness, after desensitizing with pinakryptol, may be developed before Nos. 1 and 2, but extreme red sensitive panchromatic plates, even when desensitized, will fog with any of the filters. The formulas of Servaes and van Duyse are criticized as being unsafe for use as directed. A table is printed giving the absorption limits in Å. of 2% and of 4% solns. of 20 different dyes with a few measurements of the transmission given by a 2% soln. C. E. K. MEES

6—INORGANIC CHEMISTRY

A. R. MIDDLETON

Reaction of alkali hydroxide with lead salts. A. OGATA AND T. KAIUN. *J. Pharm. Soc. (Japan)* No. 492, 75-81(1923).—The reaction between $\text{Pb}(\text{NO}_3)_2$ and alkali hydroxide is not so simple as general textbooks give. To a definite amt. of $\text{Pb}(\text{NO}_3)_2$ soln. (4-7%), various amts. of CO_2 -free N NaOH were added, and the color reactions with phenolphthalein were observed from 5 min. to 3 weeks. The ppt. formed in each case was analyzed. When a small amt. of very weakly alk. soln. is added to a large amt. of $\text{Pb}(\text{NO}_3)_2$ soln., the ppt. redissolves on shaking; with N NaOH, a white cryst. ppt. is formed. The following reaction proceeds as long as this ppt. is formed: $\text{Pb}(\text{NO}_3)_2 + \text{NaOH} = \text{Pb}(\text{OH})\text{NO}_3 + \text{NaNO}_3$; the supernatant fluid does not show alk. reaction. When more alkali is added, the ppt. becomes more or less obscure, and gives a milky effect to the soln. which now shows a brownish purple color with the indicator. On filtration the coloration is shown to be due to a stain in the floating particles, and the filtrate is still colorless. When enough alkali is added to make the pure filtrate alk. toward the indicator the following reaction is completed: $3\text{Pb}(\text{OH})\text{NO}_3 + 2\text{NaOH} = (\text{PbO})_2\text{Pb}(\text{OH})\text{NO}_3 + 2\text{NaNO}_3 + 2\text{H}_2\text{O}$. A completion of the reaction requires considerable time, since $\text{Pb}(\text{OH})\text{NO}_3$ is exceedingly insol. With more alkali the following reaction takes place: $\text{Pb}(\text{NO}_3)_2 + 4\text{NaOH} = \text{Pb}(\text{ONa})_2 + 2\text{NaNO}_3 + 2\text{H}_2\text{O}$. $\text{Pb}(\text{NO}_3)_2$ should not be used for the prepn. of $\text{Pb}(\text{OH})_2$. With $\text{Pb}(\text{AcO})_2$, since basic Pb acetate is not so insol. as the nitrate, the hydroxide free from acid radical can be obtained easily. The resulting hydroxide is probably $2\text{PbO} \cdot \text{H}_2\text{O}$ instead of $\text{Pb}(\text{OH})_2$ (cf. Schaffner, *Ann.* 51, 175). S. T.

Electron theory of valency applied to coördination compounds. C. H. SPIERS. *Chemistry and Industry* 42, 534-8(1923).—Lowry's (*C. A.* 17, 2240) assumption that an atom completes its shell to that of the inert gas immediately following is not sufficient. It is necessary to assume that, under certain circumstances, an atom will complete its shell to a higher or lower stable number. It is also suggested that the innermost pair of electrons, both of the central atom and of the coördinated atoms, or groups may be utilized to help the completion of the shell of the central atom (cf. *C. A.* 16, 1180). Numerous compds. are cited as illustrations. D. MACRAE

Plausible error in the theory of coördination. T. M. LOWRY. *Chemistry and Industry* 42, 623-4(1923); cf. *C. A.* 17, 2240.—The proposal of Spiers (preceding abstr.) to complete the outer shell by the expedient of removing the two K-electrons to that shell ignores the enormous expenditure of energy required for such a transfer. In Ni the K-electrons are closely adjacent to a nuclear charge of 28 units, while there are 8 L-electrons, 8 M-electrons and, in a coördinated compd., 16 N-electrons (some of them shared) in higher energy levels. To turn a K- into an N-electron would require at

least 6000 volts, *i. e.*, an expenditure of energy of the order of 3×10^8 cal. per g.-atom.

Stability of coordination compounds. T. M. LOWRY. *Chemistry and Industry* **42**, 711–5(1923); cf. *C. A.* **17**, 2398.—Two types of coordination are distinguished: (A) *Centric*, in which the main factor is completion of the outer shell of electrons around a metal atom and stability depends chiefly on the nature of the central atom. This type includes the majority of the compds. studied by Werner. (B) *Cyclic*, in which the principal factor is completion of a ring by linking up a metallic cation with a multipolar anion, and stability depends on the nature of both ring and metallic ion. This type was disclosed by Chugaev and developed principally by Morgan. The smallest metal atoms, Li, Be, Al, appear to form the most stable compds. as if the chelate group could grasp a small object more firmly than a large one. In conjugated systems the max. of stability is reached in six-atom rings, the polarities of which are identical with those of aromatic compds.; in satd. ring systems when a 5-atom ring is formed. Conjugated 4-atom rings are less stable and the coordinated metal is usually ionizable. Many examples are structurally formulated.

Existence of ammonium hydroxide in solution. T. S. MOORE. *Chemistry and Industry* **42**, 641–2(1923); cf. *C. A.* **17**, 2246.—Continues the controversy with Cayen.

The chemistry of thorium. V. I. SPITZIN. *J. Russ. Phys. Chem. Soc.* **49**, 357–70 (1917).—The object of this work was to study the soly. of the insol. and difficultly sol. Th compds. For this purpose both the Th emanation method of Panets and Gebezi and the β method of Strett, Fletcher and Joly were used. The β method was finally given the preference owing to greater speed and ease of manipulation. The accuracy was from 1 to 2%. The compds. used in these expts. were carefully purified. Solubilities are in mg. ThO₂ per l. at 25°. ThO₂: *N* H₂SO₄ 2.0; *N* HNO₃ 0.6; *N* HCl 0.5; 0.8 *N* C₂H₅O₄ 0.3; H₂O < 0.02; *N* NaOH < 0.05; *N* Na₂CO₃ < 0.03; *N* K₂CO₃ < 0.02; Th(C₂O₄)₃·6H₂O: H₂SO₄ 1.18 *N*, 120; 0.98 *N*, 108; 0.9 *N*, 90; 0.58 *N*, 60; 0.49 *N*, 53; 0.48 *N*, 46; 0.40 *N*, 43; 0.20 *N*, 18; 0.10 *N*, 12; 0.06 *N*, 6.9; 0.03 *N*, 3; 0.02 *N*, 2; 0.007 *N*, 0.8. H₂SO₄ satd. with C₆(C₂O₄)₄·10H₂O at 25°: 0.9 *N*, 43; 0.63 *N*, 19; 0.47 *N*, 15; 0.1 *N*, 4; 0.05 *N*, 3; 0.014 *N*, 0.9. HCl: 1.0 *N*, 24; 0.82 *N*, 21; 0.64 *N*, 16; 0.48 *N*, 8.5; 0.38 *N*, 7; 0.23 *N*, 4.7; 0.09 *N*, 1.7; 0.04 *N*, 0.6. HNO₃: 1.0 *N*, 33; 0.78 *N*, 14.4; 0.47 *N*, 10.1; 0.24 *N*, 4.5; 0.06 *N*, 1.3; 0.016 *N*, 0.3. (NH₄)₂C₂O₄·H₂O: 0.0006 *M*, 2.3; 0.0010 *M*, 4; 0.0025, 10; 0.005, 40; 0.0075, 70; 0.0100, 100; 0.0150, 180; 0.0200, 340; 0.0250, 450; 0.0300, 600; 0.0410(?), 410(?); 0.0500, 1000; 0.0600(?) 5550(?). *Soly. in various salts*: NaCl 0.1 *N*, 0.2; Na₂SO₄ 0.1 *N*, 0.6; KHSO₄ 0.5 *N*, 30; KHSO₄ 1 *N*, 77; NH₄Cl 0.1 *N*, 0.3; (NH₄)₂SO₄ 0.1 *N*, 1.0; H₂O 0.07; the data show that for a given acid the soly. of Th oxalate increases with the concn. of the acid. The soly. in H₂SO₄ is about 5 times that in HNO₃ or HCl. N. I. Valdena studied the soly. of Th oxalate in different acids 0.5 *N* with the following results: H₂SO₄ 55; HCl 12; HNO₃ 11; HBr 11.5; HI 11.2; CCl₃COOH, 12; HClO₄ 13; H₂CrO₄ 11; H₃BO₃ 0.10; C₂H₅IO₄ 4. In the acids HCl to H₂CrO₄ which in normal soln. are dissociated to the extent of about 90% the soly. of Th citrate is about const. The solubilities in H₂SO₄ and C₂H₅IO₄ are undoubtedly anomalous owing to formation of addn. compds. analogous to Ti and Zr. The soly. of Th oxalate in (NH₄)₂C₂O₄ is not uniform but at certain concns. breaks in the soly. curves occur, *i. e.*, between 0.0025 and 0.005 and between 0.015 and 0.0200. In salt solns. the soly. of ThO₂ is small, but greater in sulfates than in chlorides. ThP₂O₄·11H₂O. H₂SO₄ 1 *N*, 53; HCl, 1 *N*, 21; HNO₃ 1 *N*, 12; K₂CO₃ 1 *N*, 250. ThF₄·4H₂O. H₂O 0.17. K₂ThF₆·4H₂O is sol. 0.4 mg. Th per liter.

P. W. PUCHER

Investigations of the chromates of thorium and the rare earths. I. System thorium oxide-chromium anhydride-water at 25°. H. T. S. BRITTON. *J. Chem. Soc.* **123**, 1429–35(1923).—Th(CrO₂)₂·3H₂O became remarkably sol. in solns. of K₂Cr₂O₇ or H₂CrO₄. Investigation of the 25° isotherm indicated this to be due to formation of an acid chromate the compn. of which by extrapolation from the phase diagram according to the residue method of Schreinmakers agreed with Th(CrO₂)₂·CrO₂·3H₂O. During pptn. of basic Th chromate by K₂CrO₄ the concn. of hydron was found to decrease until pptn. began but to remain const. during the greater part of pptn. The concn. required for pptn. of basic chromate is that required for pptn. of Th(OH)₄ by alkali. Hence it is concluded that the basic chromates are adsorption compds. of hydroxide and chromate. No basic chromate of definite compn. was found.

A. R. M.

Action of sodium hyposulfite on cupric chloride in aqueous solution. J. B. FIRTH AND J. HIGSON. *J. Chem. Soc.* **123**, 1515–9(1923).—At temps. up to 30°, for low concns. of Na₂S₂O₄ (CuCl₂ in excess) the chief reactions are $2\text{CuCl}_2 + \text{SO}_2 + 2\text{H}_2\text{O} = \text{Cu}_2\text{Cl}_2$

+ H_2SO_4 + 2HCl and 6CuCl_2 + $\text{Na}_2\text{S}_2\text{O}_4$ + $4\text{H}_2\text{O}$ = $3\text{Cu}_2\text{Cl}_2$ + 2NaCl + $2\text{H}_2\text{SO}_4$ + 4HCl . In slight excess of $\text{Na}_2\text{S}_2\text{O}_4$ the Cu_2Cl_2 is further reduced, $\text{Na}_2\text{S}_2\text{O}_4$ + Cu_2Cl_2 = 2Cu + 2NaCl + 2SO_2 ; and in further excess of $\text{Na}_2\text{S}_2\text{O}_4$, Cu + $\text{Na}_2\text{S}_2\text{O}_4$ = CuS + Na_2SO_4 . At 50–75° the final product is Cu_2S mainly, if CuCl_2 is present in excess, and this is converted to CuS by excess of $\text{Na}_2\text{S}_2\text{O}_4$. Owing to the continuous change of conditions as the reaction proceeds, no simple set of equations can represent the complete phenomena.

A. R. M.

Mixed crystals and double salts: comparison of systems containing water, ammonium chloride, and a chloride of manganese, iron cobalt, nickel and copper. A. C. D. RIVETT AND F. W. J. CLENDINNEN. *J. Chem. Soc.* 123, 1634–40 (1923); cf. *C. A.* 15, 3952 and 17, 3272 (Mn); 16, 2647; 17, 3144 (ferric).—The general case is discussed of mixed-crystal formation. Observations on the system NH_4Cl – CuCl_2 – H_2O at 25° and at 0° are set forth together with the phase diagram. It is concluded that "molecular" compds. and double salts, such as $2\text{NH}_4\text{Cl} \cdot \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $2\text{NH}_4\text{Cl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$ are really mixed crystals.

A. R. M.

Germanium. VI. Metallic germanium. Reduction of germanium dioxide. Preparation of fused germanium. Physical and chemical properties. L. M. DENNIS, KATHARINA M. TRESSLER AND F. E. HANCK. *J. Am. Chem. Soc.* 45, 2033–47 (1923); cf. *C. A.* 17, 2682.—This article deals with the dehydration of GeO_2 , the reduction of GeO_2 by Al and by H, the prepn. of fused Ge, the behavior of Ge when heated in H, the m. p., sp. gr., hardness, crystal form, elec. resistance, thermoelec. power, mol. inversion, and sprouting of Ge, and the behavior of the metal toward various gases, liquid reagents and molten solid reagents.

L. T. F.

Silicon hydrides. XVI. The higher hydrides. ALFRED STOCK, PAUL STIEBELER AND F. ZEIDLER. *Ber.* 56B, 1695–1705 (1923); cf. *C. A.* 17, 2682.—In the previous work about 20 cc. of a mixt. contg. hydrides higher than Si_2H_6 had been accumulated. This was submitted to the usual procedure in the vacuum app. with exclusion of air, moisture, fat, and, for the most part, light. As a result of decompn. during several years standing protected from light 2.5 cc. H_2 was present. The temp. was slowly raised from –120° to 0° and the following condensates were obtained: –185°, 0.5 cc. nearly homogeneous Si_2H_6 ; –120°, 10.1 cc. chiefly Si_4H_{10} ; –70°, 7.7 cc. mostly Si_4H_{10} ; –20°, 1.5 cc. of 0° tension 1.5 mm. In the flask remained 1.5 cc. which was next distd. at room temp. Previous data for Si_4H_{10} were confirmed. For Si_4H_{10} were found: 0° tension, 8.1 mm.; b_{25} , 109°; liquid d. at 0°, 0.825. It also is quite stable but decomposes in daylight more rapidly than Si_2H_6 . No evidence of isomers was found. With Na–Hg decomp. as in light but much more rapidly into lower hydrides, and higher, apparently unsatd. hydrides. Pure Si_4H_{10} m. –90°; reacts toward CHCl_3 and CCl_4 like Si_2H_6 . The –20° fraction stood at room temp. several months and decompd. considerably, contg. 1.4 cc. SiH_4 and 7.7 cc. Si_2H_6 (gas vols.). The residue was sepd. (–50–0°) into 30 fractions of about 0.05 cc. each of 0° tensions > 2–0.8 mm. Attempts to fractionate further by m. p. control gave finally a fraction melting –80.9–77.8° of av. mol. wt., 169. Si_2H_6 = 154; Si_4H_{10} = 184. More than 2 compds. were present but apparently only satd. hydrides; presence of isomers was indicated. This mixt. was still more unstable than Si_4H_{10} and its spontaneous decompn. is an express photochem. reaction. The residue from the original fractionation was still more unstable than the preceding. It differed from it only slightly in tension and may have been nearly pure Si_4H_{14} . Originally colorless, it became yellow after standing several months in diffused light. After removal of the volatile products of decompn. a viscous yellow residue remained which gradually solidified while giving off small amts. of the volatile hydrides. Its external appearance indicated crystn. but examn. proved absence of crystals. Analysis by decompn. into Si and H at 1000° indicated $\text{SiH}_{1.2}$; by decompn. in vacuum with 5% NaOH, $\text{SiH}_{1.12}$. Toward Br_2 it acted as an unsatd. compd. but SiBr_4 and H_2 , but no HBr , were formed.

A. R. MIDDLETON

Acid borates of sodium. I. F. PONOMAREV. *J. Russ. Phys. Chem. Soc.* 49, I, 229–40 (1917).—By employing the principle established by Tamman (*C. A.* 8, 2971) P. succeeded in prepg. cryst. borates contg. a greater proportion of B_2O_3 than that in borax ($\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$). This was accomplished by heating fused mixts. of borax and anhyd. B_2O_3 in a Pt boat placed horizontally inside of a hard-glass test-tube. The heating being restricted to one end of the boat, a slowly falling temp. gradient was obtained along the fused mass, and the crystn. of the desired borates started at the point possessing the optimum temp., which lay in the middle region between the molten fluid at the heated end and the solid vitreous portion at the cold end. Since at the temp. of formation of the cryst. nuclei the mixt. is extremely viscous and the motion of the crystals very slow, it was possible to measure, with a thermocouple, the limiting

temps. of the cryst. formations. Chem. and crystallographic studies were made of mixts. of the oxyborates $\text{Na}_2\text{O} \cdot 3\text{B}_2\text{O}_3$ and $\text{Na}_2\text{O} \cdot \text{AB}_2\text{O}_4$ so obtained. W. A. PERLZWEIG

Lead-acetato-(oxalato)-complexes and basic lead salts. R. WEINLAND and F. PAUL. *Z. anorg. allgem. Chem.* 129, 243–62; cf. C. A. 17, 34. —W. and P. describe the prepn. of the following compds.: diacetatodiplumbodithionate $[\text{Pb}_2(\text{ac})_2]\text{S}_2\text{O}_6$, diacetatodiplumbopierate $[\text{Pb}_2(\text{ac})_2][\text{C}_2\text{H}_3(\text{O})_2\text{O}_2] \cdot 2\text{H}_2\text{O}$, diacetatotriplumbonitrate $[\text{Pb}_3(\text{ac})_3](\text{NO}_3)_3$, diacetatodiplumbobromate $[\text{Pb}_2(\text{ac})_2][\text{Br}(\text{O})_2]$, oxalatodiplumbopercarbonate $[\text{Pb}_2(\text{ox})_2][\text{C}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}]$, oxalatodiplumbonitrate $[\text{Pb}_2(\text{ox})_2][\text{NO}_3] \cdot 2\text{H}_2\text{O}$, trioxalatotetraplumbopercarbonate $[\text{Pb}_4(\text{ox})_4][\text{C}(\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}]$, dioldiplumbobichlorate $[\text{Pb}_2(\text{OH})_2][\text{ClO}_3] \cdot 1\text{H}_2\text{O}$, tetroltriplumbobichlorate $[\text{Pb}_4(\text{OH})_4][\text{ClO}_3]_2$, dioldiplumbodithionate $[\text{Pb}_2(\text{OH})_2]\text{S}_2\text{O}_6 \cdot 1\text{H}_2\text{O}$, dioldiplumbobromide $[\text{Pb}_2(\text{OH})_2]\text{Br}_2$, dioldiplumbotetracyanonickelate $[\text{Pb}_2(\text{OH})_2][\text{Ni}(\text{CN})_4]$, dioldiplumbonitroprussiate $[\text{Pb}_2(\text{OH})_2][\text{Fe}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O}$, tetroltriplumbodithionate $[\text{Pb}_4(\text{OH})_4]\text{S}_2\text{O}_6 \cdot 0.5\text{H}_2\text{O}$, tetroltriplumbobromide $[\text{Pb}_4(\text{OH})_4]\text{Br}_2$, tetroltriplumbotetracyanonickelate $[\text{Pb}_4(\text{OH})_4][\text{Ni}(\text{CN})_4]$, tetroltriplumbobromate $[\text{Pb}_4(\text{OH})_4][\text{Br}(\text{O})_2]$, basic bromate $[\text{Pb}_2(\text{OH})_2] \cdot (\text{BrO}_3)_2$, dioldiplumbobromate $[\text{Pb}_2(\text{OH})_2][\text{Br}(\text{O})_2]$, dioloxotriplumbobromate $\text{Pb}(\text{BrO}_3)_2 \cdot 2\text{PbO} \cdot 1\text{H}_2\text{O}$, trioxotetraplumbodichromate $4\text{PbO} \cdot 2\text{CrO}_3$, dioloxotriplumbodichromate $3\text{PbO} \cdot 2\text{CrO}_3$, basic nitrite $3\text{PbO} \cdot \text{N}_2\text{O}_5 \cdot 0.5\text{H}_2\text{O}$, di-(dioldiplumbo)-chlorateferricyanide $[\text{Pb}_2(\text{OH})_2][\text{ClO}_3][\text{Fe}(\text{CN})_6]$ (2 forms), di-(dioldiplumbo)-bromateferricyanide $[\text{Pb}_2(\text{OH})_2][\text{BrO}_3][\text{Fe}(\text{CN})_6]$ (2 forms), di-(dioldiplumbo)-tetroltriplumbobromateferricyanide $[\text{Pb}_4(\text{OH})_4][\text{Fe}(\text{CN})_6]$, di-(dioldiplumbo)-hypophosphiteferricyanide $[\text{Pb}_2(\text{OH})_2][\text{P}(\text{H}_2\text{O})_2][\text{Fe}(\text{CN})_6]$, dioldiplumbo- μ -oldioldiplumboferricyanide $[\text{Pb}_4(\text{OH})_4][\text{Fe}(\text{CN})_6]$ (2 forms), tetroltriplumbo- μ -oldioldiplumboferricyanide $[\text{Pb}_4(\text{OH})_4][\text{Fe}(\text{CN})_6] \cdot 8\text{H}_2\text{O}$, diacetatodiplumbobichlorate $[\text{Pb}_2(\text{OH})_2(\text{ac})_2][\text{ClO}_3] \cdot 2.5\text{H}_2\text{O}$, dioldiacetatotriplumbobichlorate $[\text{Pb}_3(\text{ac})_3] \cdot (\text{ClO}_3)_2[\text{ClO}_3] \cdot 3\text{H}_2\text{O}$, phosphotriplumbobromide $2\text{PbBr}_2 \cdot \text{Pb}(\text{H}_2\text{O})_2 \cdot 1\text{H}_2\text{O}$, phosphotriplumbobichloride $\text{PbCl}_2 \cdot \text{Pb}(\text{H}_2\text{O})_2 \cdot 1\text{H}_2\text{O}$, lead chloride monohydrate $\text{Pb}(\text{ClO}_3)_2 \cdot 1\text{H}_2\text{O}$, dilead thiocyanate monohydrate $2\text{Pb}(\text{CNS})_2 \cdot 1\text{H}_2\text{O}$. The authors give the constitution of the interesting group of basic ferricyanides. There were 2 cases of isomerism found. The various reactions of the picrates and bromates demonstrate the existence of acetatoplumbo cations. Compds. were also found having lead-oxalato cations. Lead-phosphito cations probably exist.

L. T. FAIRHALL

Compounds of aluminum bromide with phosphorus bromides and organic bromides. V. A. PLOTNIKOV. *J. Russ. Phys. Chem. Soc.* 48, 1891–6 (1916). —A compd., $\text{AlBr}_3 \cdot \text{PBr}_3 \cdot \text{EtBr}$, is obtained by the addn. with cooling of a soln. of PBr_3 in EtBr to a similar soln. of AlBr_3 . This compd. is, unlike its constituents, stable above 150° , decompn. occurring at 230° , with evolution of HBr and formation of some pentabromoethane. The complex is immediately decompd. by water, in which it is completely sol., and the entire Br content may be pptd. by AgNO_3 , EtOH being identifiable in the soln. A similar compd., $\text{AlBr}_3 \cdot \text{PBr}_3 \cdot \text{EtBr}$, m. 160° (decompn.), may be obtained by substituting PBr_3 for PBr_3 in the above reaction, while a third compd., $\text{AlBr}_3 \cdot \text{PBr}_3 \cdot \text{CMeBr}_2$, m. 134° , may be obtained by substituting ethylidene dibromide for EtBr . AlBr_3 and PBr_3 , if mixed in CS_2 soln., form a compd., $\text{AlBr}_3 \cdot \text{PBr}_3$, decomp. at 100° . J. C. S.

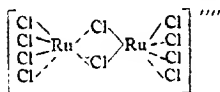
The structure of complex compounds. V. A. PLOTNIKOV. *J. Russ. Phys. Chem. Soc.* 48, 1896–1905 (1916). —The structure of complexes of EtBr with the bromides of Al and P , such as $\text{AlBr}_3 \cdot \text{PBr}_3 \cdot \text{EtBr}$ (preceding abstr.), is discussed. The combination of mols. to form complexes is explained as being due to the action of electrons contained in various atoms of the mol., and the mols. combined together to form a complex exert a profound influence on each other. The result of this is to increase the reactivity of these groups, and, if mols. of water enter the complex, hydrolysis of its constituents takes place with abnormal rapidity and completeness. J. C. S.

Chlorine salts of rhodium. A. GUTHRIE and H. BERTSCH. *Z. anorg. allgem. Chem.* 129, 67–82 (1923). —The prepn. and properties of 24 addn. compds. of Rh chloride and org. NH_4 chlorides are described and their structures discussed. Solns. of the components in aq. HCl were mixed, the concns. in each case being adjusted so that pptn. did not occur until after evapn. in a desiccator at room temp. The products are highly colored and sol. in H_2O , HCl , and EtOH , but are gradually decompd. by H_2O at higher temps. When heated they sinter over a wide temp. range, and decomp. before melting. The following substituted NH_4 hexachlororhodiums were prepd: dimethylammonium, $(\text{Me}_2\text{NH})_2(\text{RhCl}_6)$, red monoclinic; trimethyl, reddish brown, shiny crystals; ethyl, garnet; diethyl, garnet; triethyl, dark red, monoclinic; propyl, carmine; isopropyl, garnet; diisopropyl, dark red, tetragonal; tripropyl, carmine, monoclinic; butyl, light red; isobutyl, carmine; diisobutyl, light red monoclinic; guanidinium, carmine; propylenediammonium, light red; pyridinium, orange-red; β -picolinium, orange-red; lutidinium, orange-red; cholidinium, red; quinolinium, carmine; isoquinolinium, dark red. Tetra-

methyltrichlorohexachlorodirhodate, $(\text{Me}_2\text{N})_3(\text{Rh}_2\text{Cl}_6)$, brown hexagonal; tetraethyl; brown-red monoclinic; dichlorotetramethylammoniumchlororhodium chloride, $[\text{C}_2\text{H}_5\text{N}(\text{Me})_3]\text{Cl}$, dark red hexagonal; and dichlorodithylenediammonium, brick-red; were also prepd. Directions are also given for the prepn. of RhCl_3 and the recovery of the Rh from the residues.

WALTER T. SELG

Halogen salts of ruthenium. A. GUTBIER. *Z. anorg. allgem. Chem.* 129, 83-8 (1923); cf. *C. A.* 9, 2196.—The following compds. were prepd. All are decompd. by H_2O . EtOH cannot be used to crystallize them, but H halides are very suitable. Propylenediammonium- μ -dichloro-octachloro-dirutheniate $[(\text{C}_3\text{H}_7\text{N}_2\text{H}_5)_2][(\text{Ru}_2\text{Cl}_8)_2]$, deep red; α -picolinium, black; isoquinolinium, red black; the 3 corresponding bromine salts, all black; the ethylene bromine salt, black; isoquinoliniumhexachlororutheniate $[(\text{C}_9\text{H}_7\text{NH})_2][(\text{RuCl}_6)_2]$, green black; triethylhexabromo, blue black opaque; isoquinoliniumhexabromo, blue black. Following Weinland (*C. A.* 16, 1716) the dirutheniate anion is formulated:



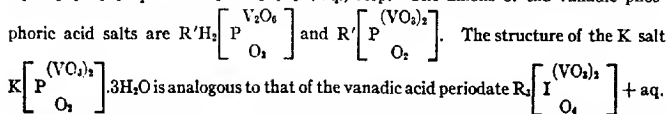
WALTER T. SELG

A new type of halogen salt of gold. A. GUTBIER. *Z. anorg. allgem. Chem.* 129, 89-92 (1923); cf. *C. A.* 5, 2845; 8, 1928.—The salts were prepd. from HAuCl_4 and HAuBr_4 and the corresponding base, the usual excess of the auric acid being avoided and the reaction taking place in presence of sufficient H halide. Products were recrystd. from dil. H halide and dried in air. The following were prepd. Dichlorodithylenediammoniumchlorauric chloride, $[\text{C}_2\text{H}_5\text{N}(\text{C}_2\text{H}_4\text{N}_2\text{C}_2\text{H}_5)_2]\text{Cl}$, yellow powder; propylenediammonium, yellow; ethylenediammoniumbromo, dark red; propylene, dark red.

WALTER T. SELG

Dipyridino derivatives of iridium. II. MARCEL DELÉPINE. *Ann. chim.* 19, 145-79 (1923); cf. *C. A.* 17, 2399.—Extended report and discussion of matter in *C. A.* 17, 1197, 1198, 1927. In addn. the prepn. of tripyridino derivs. is described. While heating 1 hr. suffices to obtain the di-Py compds., long heating is required to obtain the former and attempts to introduce more than 3 mols. of Py failed. When 2.75 g. of the orange *cis*- $[\text{IrPy}_2\text{Cl}_2]\text{K}$ in 50 g. water was refluxed on the water bath with 6 cc. of pyridine, crystals began to sep. after 6 hrs and increased in amt. largely during the ensuing 30 hrs.; after heating 20 hrs. more a second cryst. product appeared. The first salt was sol. in CHCl_3 , the second insol. The same result was obtained by heating 4 hrs. at 130° with 78-9% yield. Both products showed the same compn., $[\text{IrPy}_2\text{Cl}_2]$, and they are considered to have Py in the 1,2,6 and 1,2,3 positions, resp. The 1,2,6 isomer is sol. in 42 pts. of CHCl_3 at 21° , more sol. in hot, slightly sol. in acetone, and hot abs. EtOH, insol. in C_6H_6 . It crystallizes from hot CHCl_3 with 2 mols. of the solvent; if a little EtOH was added it crystd. with 1 CHCl_3 . The same property was earlier observed in thiosulfocarbonates and xanthates of Co (*C. A.* 2, 2691; 14, 3026). The 1,2,3 isomer was sol. only in boiling 58% Py aq. soln. From the mother liquor of the prepn. at 100° was obtained an amorphous yellow mass of compn. corresponding to IrPy_2Cl_2 . The red *trans*- $[\text{IrPy}_2\text{Cl}_2]\text{K}$ was heated 4 hrs. at 130° with double its wt. of 58% Py aq. soln. As with the orange isomer, two cryst. products formed, of which one was clearly identical with the above 1,2,6 tripyridino salt; the other of orange-red color was insol. in CHCl_3 and sol. in hot Py soln. but, unlike the above 1,2,3 compd. was decompd. by Py.HCl into a red salt of Py and a salt of an Ir complex not yet detd. A. R. M.

Vanadic acid iodates, periodates and a few phosphates with a note on the alkali-metric determination of vanadic acid. ARTHUR ROSENHEIM and KUNG HSÜ YANG. *Z. anorg. allgem. Chem.* 129, 181-95 (1923).—R. and Y. describe the prepn. and properties of the Na, K, and NH_4 salts of vanadic acid iodate, vanadic acid periodate and the NH_4 and K salts of vanadic acid phosphoric acid. The former have the general formula $\text{R}_2\text{O} \cdot \text{V}_2\text{O}_5 \cdot 2\text{I}_2\text{O}_5 \cdot \text{aq.}$ and $3\text{R}_2\text{O} \cdot 2\text{V}_2\text{O}_5 \cdot \text{I}_2\text{O}_7 \cdot \text{aq.}$, resp. The anions of the vanadic phosphoric acid salts are $\text{R}'\text{H}_2 \left[\text{P} \begin{array}{c} \text{V}_2\text{O}_6 \\ \text{O}_3 \end{array} \right]$ and $\text{R}' \left[\text{P} \begin{array}{c} (\text{VO}_2)_2 \\ \text{O}_2 \end{array} \right]$. The structure of the K salt



It was found possible to carry out the somewhat difficult analysis of these substances

by alkalimetric titration. Phenolphthalein was found not suitable but very good agreement was secured by using α -naphtholphthalein as an indicator. L. T. FAIRHALL.

Formation of manganese carbide from carbon dioxide and manganese. E. MÜLLER AND H. BARCK. *Z. anorg. allgem. Chem.* 129, 321-2 (1923).—In preliminary studies of the influence of metals on the velocity of $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$ it was found that Cu and especially Fe and Cr greatly accelerated formation of CO but Mn acted entirely differently. When a mixt. of 43.3 cc. CO_2 and 43.8 cc. H_2 was led over powd. Mn at 800° till the gas vol. became const. (2 hrs.), the gas residue, 43.6 cc. proved to be pure H_2 contg. neither CO_2 nor CO. The Mn was changed partly into green MnO partly into Mn_3C . The latter gave pure CH_4 when boiled with water. A. R. M.

Interactions of thiocyanates and ferric salts. J. CLARENS. *Bull. soc. chim.* 33, 988-91 (1923).—Controverses interpretations of these reactions by Durand and Bailey (*C. A.* 17, 2998). Evidence is presented that excess of FeCl_3 in HCl soln. forms $(\text{HSCN})_2$ which does not react with FeCl_3 until slowly depolymerized. A. R. M.

Solubility. VIII. Solubility of cobaltamines. FRITZ EPIRAIM. *Ber.* 56B, 1530-42 (1923); cf. *C. A.* 17, 912.—On account of the unusually large possibilities of systematically varying their compn. these compds. offer excellent material for studying the relation between structure and soly. The solubilities were detd. at room temp. (17.5 – 23°) of salts of the following classes. (1) Tervalent cations: $[\text{Co}(\text{NH}_3)_6]$, 14 salts; $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]$, 11 salts; $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]$, 5 salts. (2) Bivalent cations: $[\text{Co}(\text{NH}_3)_5\text{Cl}]$, 14 salts; $[\text{Co}(\text{NH}_3)_4\text{Br}]$, 12 salts; $[\text{Co}(\text{NH}_3)_3\text{I}]$, 7 salts; $[\text{Co}(\text{NH}_3)_3\text{NO}_2]$, 13 salts; $[\text{Co}(\text{NH}_3)_2\text{NO}_2]$, 14 salts. (3) Univalent cations: *cis*- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]$, 13 salts; *trans*- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]$, 13 salts. (4) Nonelectrolytes: 8 salts. Hydrolysis did not affect the detns. at the temps. chosen. The data are discussed from the viewpoint that solvate formation is an essential preliminary to soln. and the effect upon this of chem. similarity of solute and solvent, similar or markedly different size of anion and cation and prevention of solvate formation by spatial occlusion of parts of the mol. capable of such formation by other parts of the mol. Many of the salts used had not been previously prepd. These *new salts* are described and method of prepn. (mostly simple metathesis) are stated. Analysis includes only detn. of Co and water in hydrated salts. The *new salts* include: $[\text{Co}(\text{NH}_3)_6](\text{SiF}_6)_3$; of $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]$: perchlorate, naphthalene- β -sulfonate (6 aq.), picrate, *improved method* for prepn. the iodide by dropwise addn. to concd. soln. of the chloride of a concd. soln. of the 6-fold wt. of KI; wash ppt. with water then with EtOH. Of $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]$: nitrate (from $[\text{Co}(\text{NH}_3)_6\text{CO}_3]$, SO_4 and HNO_3), picrate, naphthalene- β -sulfonate (6 aq.). Of $[\text{Co}(\text{NH}_3)_5\text{Cl}]$: perchlorate, picrate, naphthalene- β -sulfonate (6 aq.), thiosulfate, oxalate. Of $[\text{Co}(\text{NH}_3)_4\text{Br}]$: iodide, perchlorate (1 aq.), thiosulfate, picrate, naphthalene- β -sulfonate (6 aq.). Of $[\text{Co}(\text{NH}_3)_3\text{I}]$: chlorate, sulfate, picrate. Of $[\text{Co}(\text{NH}_3)_3\text{NO}_2]$: iodide, chlorate, perchlorate, silico-fluoride, picrate, naphthalene- β -sulfonate (3 aq.). Of $[\text{Co}(\text{NH}_3)_2\text{NO}_2]$: iodide, perchlorate, picrate, naphthalene- β -sulfonate (3 aq.). Of *cis*- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]$: bromide, perchlorate, fluosilicate picrate. Of *trans*- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]$: chlorate, perchlorate, fluosilicate, picrate. A. R. M.

Alkaline copper oxide solutions. III. W. TRAUBE. *Ber.* 56B, 1653-6 (1923); cf. *C. A.* 16, 1934; 17, 72.—The arguments previously advanced for the constitution of the poly-OH and biuret compds., viz., that Cu is contained in both anion and cation, are reinforced by the prepn. of two new salts, $[\text{Ag}(\text{NH}_3)_2][(\text{C}_2\text{O}_2\text{N}_3\text{H}_2)_2\text{Cu}]$ and $[\text{Ag}(\text{en})_2][(\text{C}_2\text{O}_2\text{N}_3\text{H}_2)_2\text{Cu}]$, both of pure red color and well crystd. From their color and mode of prepn. they must be regarded as analogs of Schiff's salt, $\text{K}_2[(\text{C}_2\text{O}_2\text{N}_3\text{H}_2)_2\text{Cu}]$. To 1.4 g. biuret was added 10 cc. of 10% NH_3 soln., or 21 cc. of 10% ethylenediamine soln., then the freshly pptd. and well washed Ag_2O from 2 g. AgNO_3 and 0.56 g., or 0.75 g. of $\text{Cu}(\text{OH})_2$. The $\text{Ag}(\text{NH}_3)_2$ salt formed granite-red crystals after standing a few hours at 0° . Yield, 2.5 g. The $\text{Ag}(\text{en})_2$ compd. was obtained by evapng. the soln., filtered through asbestos, in high vacuum over H_2SO_4 some hours until crystn. began. Yield, 1.2 g. ruby-red short prisms. An appended paragraph continues the polemic with Hess and Messmer (*C. A.* 17, 1217, 2500). A. R. M.

Sulfamide. W. TRAUBE AND E. REUBKE. *Ber.* 56B, 1656-63 (1923).—This compd. can be conveniently prepd. in large amts. from NH_3 and SO_2F_2 . As $\text{O}_5\text{S}(\text{NH}_2)_2$ is the only N-contg. product detectable, the crude product is readily obtained pure and yields are much larger than when SO_2Cl_2 is used. Three methods of prepn. are described which gave, resp., 54, 90 and nearly 100% of the theoretical yield. Most convenient is shaking SO_2F_2 (gas) with at least a 4-fold excess of 25% NH_3 aq. soln. contg. CaCO_3 in considerable excess, to ppt. HF; 1 l. is absorbed in about 15 min. The filtered liquid is concd. in ordinary vacuum at 40° and then, still liquid because of its content of $\text{SO}_2(\text{NH}_2)_2 \cdot \text{NH}_3$,

brought into high vacuum over H_2SO_4 , when it quickly solidifies. A single recrystn. gives a pure product, m. 92° . Yield, about 15 g. from 4 l. of SO_2F_2 . The following gave 4-5 l. of SO_2F_2 . In an iron tube 28×3.5 cm., provided with screw-caps the upper having a welded-in delivery tube, 50 g. crude FSO_3H (distn. of CaF_2 with fuming H_2SO_4) is treated with 45 g. dried BaF_2 with thorough stirring. The mixt. is let stand some time protected from moisture, then carefully heated to complete the reaction and remove HF , then evacuated and heating and evacuation repeated again. Good yield depends on greatest possible removal of HF . The upper cap is screwed on, the tube heated until air is displaced, then connected to a gasometer and heated strongly. The gas can be kept in glass gasometers over water for considerable periods without much loss. Evidence is presented that in aq. soln. under the influence of strong bases sulfamide under-

goes rearrangement into an acid form, $\text{O}_2\text{S} \begin{smallmatrix} \text{NH}_2 \\ \diagup \\ \text{NH}_2 \end{smallmatrix} \rightleftharpoons \text{O}=\text{S} \begin{smallmatrix} \text{OH} \\ \diagup \\ \text{NH}_2 \end{smallmatrix}$. It absorbed dry

NH_3 , at 20° nearly 1.5 mol., at -20° more than 5 mols. per mol., forming a liquid compd. having more than 150 times the cond. of aq. soln. of $\text{SO}_2(\text{NH}_2)_2$ contg. greater concn. of this compd. The cond. of an aq. soln. of NH_3 was increased 25-fold when a practically non-conducting aq. soln. of the equimol.-amt. of sulfamide was added to it. An NH_4 salt could not be isolated but various other salts could be prepd. and from all of these sulfamide could be obtained again in good yield. In consequence of hydrolysis of not over 15% of the employed sulfamide to aminosulfonic acid, alkali and alk. earth salts could not be prepd. pure in aq. soln. but could in EtOH soln. The Na , K , Li , Ba , $[\text{Cu}(\text{NH}_3)_4]$ and $[\text{Cuen}_2]$ salts were prepd. and analyzed. The action of sulfamide on various org. compds. was investigated, mostly without positive result. *Benzylidene sulfamide*, $\text{NH}_2\text{SO}_2\text{N}:\text{CH}.\text{C}_6\text{H}_5$, was obtained by heating for several hrs. on a water bath equal wts. of sulfamide and benzaldehyde in concd. EtOH soln. with some dehydrated CuSO_4 and evapg. the filtered soln. to crystn. To remove unchanged sulfamide required 2 recrystns. from MeOH followed by 3 from C_6H_6 . Yield, 8-10% of theory. M. p., 135° . Little sol. in water and decompd. by boiling water. A new inorg. derivative of sulfamide, *monochlorosulfamide*, $\text{SO}_2(\text{NH}_2)(\text{NH}.\text{Cl})$, was prepd. by dropping 6% HClO soln. into well cooled concd. aq. soln. of sulfamide with continuous shaking until equiv. amts. were present. The ice mush was allowed to melt and the liquid evapd. to crystn. in vacuum. The product was extd. with Et_2O . It melts at 66° and gives all the reactions of acid amides chlorinated on N. Easily sol. in water, EtOH , Et_2O , CHCl_3 ; alkalis and NH_3 evolve N. A. R. M.

Precipitation of metals of the odd series of group II of the periodic system from their aqueous solutions by hydrogen at high pressures. V. N. IPATIEV AND A. STARYNKEVICH. *Ber.* 56B, 1663-7(1923).—See C. A. 9, 766; 17, 2217. A. R. MIDDLETON

Oxidation of alkali cyanides in aqueous solution. LUDWIG HESS. *Ber. pharm. Ges.* 33, 178-81(1923).—An example of the method is indicated in the following: In 365 cc. H_2O dissolve 102 g. NaOH and 72 g. NaCN , and cool the soln. to 15° . Treat with 74 g. of Cl liberated from calcd. amts. of HCl and KMnO_4 at a temp. not exceeding 20° . Sep. the NaCNO formed by suction on a porous plate, wash with alc. and dry. Yield 90-5%. The oxidation of KCN and $\text{K}_4\text{Fe}(\text{CN})_6$ are some of the other reactions considered. W. O. E.

Lithium-ammonia. F. BENOIT. *Bull. soc. chim.* 33, 908-17(1923).—The Li employed was prepd. by electrolysis of equal parts of LiCl and KCl . Its compn. was Li, 99.1%, K, 0.67%, a trace of Fe; the remainder was O and N. Both the method of Joannis (*Ann. chim. phys.* 7, 1-129(1906)) and the isotherm method of Biltz and Hürtig indicated Li_4NH_3 or $\text{Li}_2.8\text{NH}_3$ as the only compd. For this $p_{\text{NH}_3} = 1$ atm. at 70.5° . The heat of formation from Li sol. and NH_3 gas is 8.67 cal. per mol. of Li. The compds. described by Moissan, LiNH_3 and Li_3NH_3 , do not exist. His results are due to a secondary reaction, $\text{Li}_2.8\text{NH}_3 = 2\text{LiNH}_3 + \text{H}_2 + 6\text{NH}_3$, the speed of which increases rapidly with temp. and may depend on the purity of the Li employed, K acting as catalyst. This point is being investigated. A. R. M.

Preparation of alkali metals. M. BUOU. *Bull. soc. chim.* 33, 994-5(1923).—The method of Hackspill (C. A. 5, 2471) is modified by evacuating with water pump only and heating electrically to 350° . When evolution of gas ceases, which is marked by fall of the manometer to about 20 mm., connection with the pump is broken by closing a stopcock or by sealing off at a constriction in the connecting tube. The alkali metal is then distd. into a receiver by gradually raising the temp. to 800° . The yield is only very slightly diminished. This method is incomparably superior to that of Erdmann and is an instructive exercise for advanced students. A. R. M.

Sublimation of aluminium chloride. E. BILMANN. *Bull. soc. chim.* 33, 995-6

(1923).—To sublime AlCl_3 for Friedel-Crafts reactions, charge a test-tube 0.35×18 cm. with 40 g. of AlCl_3 , surround the lower part with a cylinder of Fe gauze, close the mouth with a cover of sheet iron and wrap the upper part of the tube with cotton cloth. Heat with a Bunsen burner and let cold water drop steadily on the cloth during heating. Time about 20 min.; yield 37–8 g.

A. R. M.

Polysulfides of the alkali metals. IV. Polysulfides of ammonium. J. S. THOMAS AND R. W. RIDING. *J. Chem. Soc.* 123, 1726–38(1923); cf. *C. A.* 12, 568. To solns. of NH_4HS in dry EtOH the amts. of S scaled, to give the pentasulfide were added and the mixts. refluxed several hours at 60° with a fine stream of H_2 continuously bubbled through. The soln. became nearly black and much H_2S was evolved. On cooling abundance of large crysts. sepd.; these were removed by suction, washed with 20 cc. cold EtOH , then 20 cc. of a mixt. of CS_2 and Et_2O and finally with Et_2O . The product decompd. in air but was stable under small pressure of NH_3 over paraffin wax. Analysis after 3 days corresponded closely to $(\text{NH}_4)_2\text{S}_5$. The crystals can be kept for long periods in a soln. of NH_3 in dry Et_2O . Attempts to prep. lower compds. by varying the proportions of NH_4HS and S gave impure pentasulfide. On heating the pentasulfide in a Paraday tube for several hours, one arm in boiling water the other in ice-salt, a yellow oil gradually collected and solidified to yellow crystals found to be $(\text{NH}_4)_2\text{S}_2$ not previously known. Pure S remained and the reaction $(\text{NH}_4)_2\text{S}_5 = (\text{NH}_4)_2\text{S}_2 + 3\text{S}$ is quant. At 25° an EtOH soln. of pentasulfide dissolves S to an extent indicated by $(\text{NH}_4)_2\text{S}_{4.17}$. Owing to decompn. all attempts to prep. higher compds. by crystn. from these solns. failed. S was added to an EtOH soln. of pentasulfide and the mixt. stored 4 mos. tightly stoppered. After this interval the solid was red and distinctly cryst. and compn. agreed well with $(\text{NH}_4)_2\text{S}_5$. All attempts to prep. Bloxatt's emmeasulfide, $(\text{NH}_4)_2\text{S}_6$, failed.

A. R. M.

Constitution of the higher oxide of nickel. O. R. HOWELL. *J. Chem. Soc.* 123, 1772–83(1923); cf. *C. A.* 17, 2244. NiO_2 decomposes directly to hydroxide without intermediate formation of Ni_2O_3 . By following the rate of decompn. of the ppt. obtained by action of alkali and hypochlorite on NiSO_4 soln., the relative amts. of Ni pptd. as Ni_2O_3 and as NiO_2 were detd. $\text{Ni}(\text{OH})_2$ is oxidized simultaneously to Ni_2O_3 and NiO_2 . The Ni_2O_3 is not oxidized to NiO_2 and therefore a limit is set to the O content of the ppt. When alkali just equiv. to the Ni is used and increasing amts. of hypochlorite, the O of the latter first enters almost quantitatively as NiO_2 then as Ni_2O_3 , the change occurring at 0.25 equiv. of hypochlorite. This is ascribed to formation of a complex, oxidation of which proceeds differently: $4\text{NiO} \rightarrow \text{Ni}_2\text{O}_3 \cdot 3\text{NiO} \rightarrow \text{NiO}_2 \cdot \text{NiO} + \text{Ni}_2\text{O}_3 \rightarrow x\text{NiO}_2 + y\text{Ni}_2\text{O}_3$. This also explains the fact that with 0.5 equiv. of hypochlorite exactly 0.5 of the Ni is pptd. as Ni_2O_3 and 0.25 as NiO_2 and $\text{Ni}(\text{OH})_2$, resp. With increasing amt. of alkali for pptn., the fraction pptd. as NiO_2 increases and is proportional to the adsorption of alkali. This is attributed to a stabilizing effect due to adsorption of alkali on the positive and the negative O linkings of the peroxide to form an inactive mol. These facts offer an explanation for the decay in activity of an O-carrying catalyst whose efficacy depends on formation and reduction of a higher oxide.

A. R. M.

Easily filtered ferric hydroxide precipitated by thiosulfate and iodate. F. L. HAHN AND MARIA HERTRICH. *Ber.* 56B, 1729–32(1923).—Acid Fe^{III} solns. are neutralized with Na_2CO_3 or NH_3 and any ppt. is dissolved by HCl ; at water-bath temp. thiosulfate soln. is added in small amts. until the soln. becomes permanently colorless. $2\text{Fe}^{+++} + 2\text{S}_2\text{O}_3^{--} \rightarrow 2\text{Fe}^{++} + \text{S}_4\text{O}_6^{--}$. Then corresponding to $2\text{Fe}^{++} + 6\text{H}_2\text{O} + 10\text{I}^- + 4\text{S}_2\text{O}_3^{--} = 2\text{Fe}(\text{OH})_3 + \text{I}^- + 2\text{S}_4\text{O}_6^{--}$, double the previously used amt. of thiosulfate soln., about 2 g. NH_4Cl , and iodate soln. in slight excess over the calcd. amt. are added and the mixt. is left on the water bath until the liquid becomes clear. The ppt. is fine-grained and requires a fine-pore filter but even with double filtration of the first portion, an ordinary filter being used, filtration is much quicker than that of $\text{Fe}(\text{OH})_3$ pptd. by NH_3 . The ppt. is so dense that amts. corresponding to over 0.5 g. of Fe_2O_3 after ignition can be assembled and washed on a 9 cm. filter. Data show that NH_4 salts are essential to prevent pptn. of basic salts of Fe. The ppt. must be ignited over the blast lamp. Ignited over a Meeker burner, wts. averaged about 0.5% high. Fe_2O_3 was not formed during ignition if reducing gases were excluded.

A. R. M.

Quantitative decomposition of native fluorspar by fusion with excess of sodium carbonate. C. C. PALIT. *Z. anorg. allgem. Chem.* 128, 350–4(1923).—The data show that decompn. is incomplete after 1 fusion but is complete after 2 fusions. The amt. decompd. in 1 fusion was increased by fineness of grinding and by the excess of carbonate employed, but not much affected by increased time of fusion. In spite of wide variation of these 3 factors, a rather const. amt. remained undecompd. by 1 fusion—about 6%

of the specimen used. It is suggested that there may be 2 modifications of CaF_2 of differing soly. Boulanger and Urbain (*C. A.* 16, 3453) similarly found Madagascar thortveitite could not be completely decompd. in 1 fusion. A. R. M.

The oxides of iron. J. B. FERGUSON. *J. Wash. Acad. Sci.* 13, 275-81(1923); cf. *C. A.* 17, 2841.—F. has found that the Fe phase in the system (H_2 , H_2O , Fe, FeO) does not contain appreciable quantities of O. The transition temp. of the FeO phase appears to be lowered by soln. of the ferro-ferric oxide in the FeO. The quadruple point lies below 577° . A value for the equil. const. at 750° was obtained by the stream method and agrees with the value obtained by interpolation from the results of Chaudron and furnishes a check on the latter. I. T. F.

Decomposition of nitric oxide when heated with metals. E. MÜLLER AND H. HARKK. *Z. anorg. allgem. Chem.* 129, 309-20(1923).—Doubt of the effectiveness of a Ag spiral to remove NO in elementary microanalysis as recommended by Dubsy (Vereinfachte quant. Mikroelementaranalyse org. Substanzen, Note 2, p. 32) led to investigation of this and other metals. At 400° freshly reduced Cu spirals decomp. NO 6-71%, depending on purity of the Cu and nature of preliminary heating of the spiral. Results were reproducible only when the spiral was heated to dark redness in a combustion tube in an atm. of MeOH or H_2 . A spiral contg. a small amt. of Zn at 400° decompd. 87-8% while one of pure Cu (traces only of C) decompd. 39-45%. With the former undecompd. NO decreased regularly with rising temp. to 500° ; with the latter maxima were found at 300° and 500° , undecompd. NO increasing at $300-400^\circ$ and decreasing at $450-500^\circ$. In the latter case N_2O was formed below 400° and the data showed another reaction, possibly formation of Cu_2NO_2 or nitride. Above 500° decompn. was complete by both spirals. Ag was practically without action at $20-200^\circ$, at 400° and at 700° . Fe, in form of a spiral of wire gauze, decompd. more quickly and at lower temp. than Cu but must be preheated in H_2 at least 1.5 hrs. Brass, no action up to 600° ; at 700° decompd. 29%. Sn, no action below its m. p. or when heated to 400° ; at 450° decomp. NO with formation of nitride; the latter is much less formed at 500° and not at all at 600° . Zn below 350° did not act; at 600° slow but nearly complete decompn. Bi decompd. 73.6% at 400° with formation of Bi_2O_3 . Pb at 600° slowly decompd. to 86.6%. Mg (shavings), action began at 500° ; rapid decrease of gas vol. at 600° due to oxide formation followed by slow decrease due to nitride formation. Cr acted like Mg. Al, only slight action below 600° ; at 600° 8% decompd. Mn, acted even at 300° ; at 400° decompn. was 68%; at 500° 100%; formation of nitride at 400° was established. Cr, no action at 700° . Ferrochrome, 60% Cr, decompd. 18.6% at 650° . PbO_2 absorbs NO at 1 atm. and room temp. completely with formation of $\text{Pb}(\text{NO}_2)_2$; at 200° 4.5 g. PbO_2 absorbed 158 cc. NO; above 200° O splits from PbO_2 and forms NO_2 . PbO decompd. only 1.7% at 650° . Pb_2O_3 does not react at room temp.; at 200° decompn. was nearly complete with formation of nitrite. V_2O_5 decompd. 11% at 400° , 100% at 500° with oxidation to V_2O_6 . A. R. MIDDLETON

Sulfurous acid and its salts. I. Decomposition of sulfurous acid and its salts in aqueous solution. F. FOERSTER, F. LANGE, O. DROSSBACH AND W. SEIDEL. *Z. anorg. allgem. Chem.* 128, 245-342(1923).—The divisions of this very extensive investigation are: (1) Historical. (2) Analytical procedures. (3) Spontaneous decompn. of H_2SO_3 at 150° , 180° , $120-5^\circ$, 100° , in sunlight at room temp.; theoretical discussion of the process; decompn. of H_2SO_3 at 100° in presence of thiosulfate; the role of hypo-sulfurous acid in the decompn. (cf. Jungfleisch and Brunel, *C. A.* 7, 3459, 3933). (4) Spontaneous decompn. of alkali bisulfites in sealed tubes at $100-50^\circ$; concd. NH_4HSO_3 soln. in open vessels, boiling and at room temp.; decompn. of alkali bisulfites in sealed tubes at $70-80^\circ$; theoretical discussion of the data. (5) Possibility of tech. employment of the above phenomena. (6) Catalytic action of Se on the first principal stage of decompn.: (a) selenosulfate and selenodithionate; (b) selenothionates of the tetra- and penta-types; oxidizing action of H_2SeO_3 on H_2SO_3 , $\text{H}_2\text{S}_2\text{O}_3$ and H_2SeSO_3 ; (c) decompn. of selenodithionate; (d) mechanism of the catalytic action of Se. Authors' summary is essentially as follows: The reaction $3\text{H}_2\text{SO}_3 \rightarrow 2\text{SO}_4 + 4\text{H}^+ + \text{S} + \text{H}_2\text{O}$ (a) has a very small velocity requiring for completion many days at 100° , and about 2 days at 150° . It is autocatalyzed by S and hydron oppositely; the positive action of S, even in case of preliminary addn. of this substance, is evident only in the beginning and is soon greatly exceeded by the negative action of hydron. As a result dil. solns. decompose more quickly than concd. and decompn. is practically complete; in concd. solns., even after long heating at 180° , decompn. is incomplete; the decompn. is completely suppressed by even $2N$ HCl as solvent. Very probably the first stage consists of (b) $2\text{HSeO}_3 \rightarrow \text{SO}_4 + \text{SO} + \text{H}_2\text{O}$, and (c) $2\text{SO} + \text{H}_2\text{O} \rightleftharpoons \text{S}_2\text{O}_3 + 2\text{H}^+$. The positive catalytic action of S arises from its generating $\text{H}_2\text{S}_2\text{O}_3$ (d) $\text{HSO}_3 + \text{S} \rightleftharpoons \text{S}_2\text{O}_3 +$

H^+ , far more rapidly than (b) and (c); this gives pentathionic acid, (c) $5\text{S}_2\text{O}_4^{*} + 6\text{H}^+ \rightarrow 2\text{S}_5\text{O}_{10}^{*} + 3\text{H}_2\text{O}$, which is degraded by HSO_3^{*} , (f) $\text{S}_2\text{O}_4^{*} + \text{HSO}_3^{*} \rightarrow \text{S}_4\text{O}_6^{*} + \text{S}_2\text{O}_3^{*} + \text{H}^+$ and (g) $\text{S}_2\text{O}_4^{*} + \text{HSO}_3^{*} \rightarrow \text{S}_2\text{O}_3^{*} + \text{S}_2\text{O}_3^{*} + \text{H}^+$, and finally the trithionic acid is saponified (h) $\text{S}_2\text{O}_4^{*} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{*} + \text{S}_2\text{O}_3^{*} + 2\text{H}^+$; all these reactions are rapid in comparison with (b) and regenerate S_2O_3^{*} which is the real positive catalyst if the hydron concn. is sufficient for (e). In accord with this theory S_2O_3 is always present during decompn. of H_2SO_5 together with anions of polythionic acids; the concns. of which far exceed that of S_2O_4^{*} ; their concns. at first increase and later decrease; the more of these intermediate products is present the more the ratio $\text{S} : \text{SO}_4$ lags behind 1:2 required by (a). The negative catalytic action of hydron consists in destroying the positive catalyst by forcing (d) to the left and so repressing (e) and that in (f) $\text{HSO}_3^{*} + \text{H}^+ : \text{SO}_3 + \text{H}_2\text{O}$ and (h) $\text{S}_2\text{O}_4^{*} + 2\text{H}^+ \rightleftharpoons 2\text{SO}_3 + \text{H}_2\text{O}$ it suppresses the only ions, HSO_3^{*} , or S_2O_3^{*} which can give rise to the decompn. According to Volhard III, in contrast to HCl , strongly catalyzes positively decompn. of H_2SO_5 . The positive catalytic action of its anion must far surpass the negative action of hydron; as I unites with SO_3 to form yellow, complex anions, such as $[\text{I}(\text{SO}_3)_4]$, the condition for decompn. of H_2SO_5 in soln. must lie in coordinative or constitutive binding of SO_3 ; such condition would be accomplished through (k) $\text{SO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HSO}_3^{*}$ and $[\text{SO}_3 \cdots \text{SO}_3] \rightleftharpoons \text{S}_2\text{O}_6^{*}$. S_2O_6 also, forms in solns. contg. SO_2 yellow complex ions like $[\text{S}_2\text{O}_6(\text{SO}_3)_2]$ but in such solns. the formation of H_2SO_5 (e) far exceeds direct formation of SO_4^{*} from such complex ions. In solns. of bisulfites, owing to smaller concn. of hydron and the consequently strong positive action of S_2O_4^{*} , decompn. is much more rapid than in solns. of H_2SO_5 of equal mol. concn. and is complete even in concd. solns. Preliminary addn. of S or polythionate considerably shortens the time. A bisulfite soln. decomposes at room temp., as at 80° or higher nearly to disappearance of bisulfite according to (b)–(h) with formation of sulfate and polythionate but without formation of free S (Principal Stage I); as these stages liberate also H^+ , acidity decreases less than HSO_3^{*} and (d) is forced to the left, when bisulfite is nearly exhausted, and, the H^+ liberated by (h) always increasing with continuous formation of SO_4^{*} , free S forms from polythionate and thus raises the acidity. (Principal Stage II). Forcing of (d) to the left increases the sulfite- S which is now present as H_2SO_4 and decomposes slowly according to (a) assisted by the catalytic action of the polythionates. Prevention of escape of SO_2 is essential. When strong bisulfite soln. is boiled in an open vessel so that by hydrolysis and loss of SO_2 it changes into bisulfite-sulfite, Principal Stage I forms only approx. equal mols. of SO_4^{*} and S_2O_3^{*} and very little polythionate. At the very small hydron concn. S_2O_4^{*} causes no marked autocatalysis and the change, essentially according to (b) and (c), is very slow. Since H^+ increases, the soln. is slightly acid when sulfite- S vanishes and now the Second Stage forms SO_4^{*} and S according to (l) $\text{S}_2\text{O}_3^{*} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{*} + \text{H}_2\text{S}$, (m) $\text{S}_2\text{O}_3^{*} + 2\text{H}^+ \rightarrow \text{SO}_2 + \text{S} + \text{H}_2\text{O}$ and (n) $2\text{H}_2\text{S} + \text{SO}_4 \rightarrow 3\text{S} + 2\text{H}_2\text{O}$ without increase of acidity or temporary enrichment in sulfite- S . Pure bisulfite and bisulfite-sulfite solns. are strongly catalyzed positively by small amts. of Se as element or as H_2SeO_4 ; only the Principal Stage I is involved. Se goes into soln. as SeSO_3^{*} and separates quant. before S begins to sep. K_2SeSO_3 and $\text{K}_2\text{Se}_2\text{O}_6$ were prepd. in pure condition, the former for the first time. The capacity for existence of selenothionates of the tetra- and penta-types was verified. Analogous to (d) is (n) $\text{SeSO}_3^{*} + \text{H}^+ : \text{HSO}_3^{*} + \text{Se}$ but Se seps. with far smaller H^+ concns. than S . Since (n) is displaced strongly toward the right by free H_2SO_5 , Se catalyzes decompn. of H_2SO_5 much less than S and must sep. toward the end of Stage I as soon as concn. of H^+ reaches about that of a corresponding amt. of H_2SO_5 . In a bisulfite soln. neither transformation of SeSO_3^{*} into $\text{Se}_2\text{SO}_6^{*}$ nor sapon. of the latter to sulfate, (o) $\text{Se}_2\text{SO}_6^{*} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{*} + \text{SeSO}_3^{*} + 2\text{H}^+$ proceeds with greater velocity than the analogous reactions of the S compds. On the contrary, the oxidizing actions of H_2SeO_4 , (p) $\text{SeO}_2 + \text{HSO}_3^{*} \rightarrow \text{SeO} + \text{SO}_4^{*} + \text{H}^+$, (q) $\text{SeO} + \text{HSO}_3^{*} \rightarrow \text{Se} + \text{SO}_4^{*} + \text{H}^+$, (r) $\text{SeO}_2 + 2\text{S}_2\text{O}_3^{*} + 2\text{H}^+ \rightarrow \text{SeO} + \text{S}_2\text{O}_6^{*} + \text{H}_2\text{O}$, (q₁) $\text{SeO} + 2\text{S}_2\text{O}_3^{*} + 2\text{H}^+ \rightarrow \text{Se}_2\text{SO}_6^{*} + \text{H}_2\text{O}$ and (q₂) $\text{SeSO}_3^{*} \rightarrow \text{S}_2\text{O}_6^{*} + \text{Se}$, were proved to be reactions of very high velocity, in (q) and (q₁) increasing with rising concn. of H^+ , which regenerate SeSO_3^{*} through the Se set free in them. The assumption, supported by numerous facts, that in bisulfite soln. (r) $\text{HSO}_3^{*} + \text{SeSO}_3^{*} \rightleftharpoons \text{HSeO}_3^{*} + \text{S}_2\text{O}_3^{*}$ and can furnish the H_2SeO_4 necessary for (p) and (q) accounts for the strong catalytic effect of Se on decompn. of bisulfite solns. in a manner which accords with all the facts. At the H^+ -concn. of a sulfite-bisulfite soln., then, H_2SeO_4 or HSeO_3^{*} would oxidize HSO_3^{*} to SO_4^{*} according to (p) and (p₁) and S_2O_3^{*} resulting, with HSeO_3^{*} , in (r) would increase. At the H^+ -concn. of a bisulfite soln., on the contrary, S_2O_3^{*} would be oxidized to tetrathionate (q), (q₁), (q₂). To such a reaction-mechanism the catalytic action of S becomes analogous if one assumes that

pentathionate formation, the decisive factor, proceeds according to (c) and (s) $\text{SO} + 2\text{S}_2\text{O}_4^{*} + 2\text{H}^{+} \longrightarrow \text{S}(\text{S}_2\text{O}_4)_2^{*} + \text{H}_2\text{O}$. Te, which so far as known, forms no stable anion analogous to SeSO_3^{*} , has no catalytic effect on decompn. of bisulfite provided it is Se-free. In division 5 of the work (cf. Bosch, *Z. Elektrochem.* **24**, 365(1918)) it is pointed out that even pure bisulfite solns. are not very stable and, as here shown, decompose with velocity increasing with time and the decompn. will be greatly accelerated by very small amts. of catalysts. SO_2 from combustion of S is likely to contain traces of S; that from roasting of pyrite to contain Se. Such decompn. has been noted in cryst. alkali sulfites, particularly in the K metasulfite, $\text{K}_2\text{S}_2\text{O}_5$. Stored stock took on a more or less yellow color and then contained considerable sulfate and S; occasionally, strong spontaneous heat-evolution accompanied formation of the yellow color. The salt was found to contain detectable amts. of Se.

A. R. MIDDLETON

Oxidation of ferrous sulfate in the air. P. K. BANERJEE. *Z. anorg. allgem. Chem.* **128**, 343-9(1923).—The velocity of oxidation was extremely slow for short periods (2-5 hrs.) in FeSO_4 alone or in mixt. with sulfates of other metals. Considerable differences were found in the velocity of oxidation over long periods (62 days). For FeSO_4 alone as well as mixts. with sulfates of Na, K, NH_4 , Mg, Zn, Cu, Mn, Ni and H_2SO_4 the data indicated a first-order reaction rather than a second and each added sulfate caused individual effects. K_2SO_4 accelerated the reaction; all the others retarded it more or less. It is concluded that the reaction is monomolecular and complicated by side reactions.

A. R. M.

Reaction between bromine and ammonium salts and its effect on the precipitation of manganese dioxide. S. G. SIMPSON. *J. Am. Chem. Soc.* **45**, 1883-91(1923).—The effect of NH_4 salt on the pptn. of MnO_2 by $\text{Br}_2\text{-H}_2\text{O}$ following a basic acetate sepn. was studied by detg. the amts. of Br_2 used up by $(\text{NH}_4)_2\text{SO}_4$, MnSO_4 and mixts. of the two under varying degrees of initial acidity and in presence of varying amts. of alkali acetate. The data show that each of the reactions is progressively retarded by increased acid and progressively accelerated by increased acetate, the effect being greater with Mn than with NH_4 . In absence of acid the reactions $2\text{NH}_4^{+} + 3\text{Br}_2 = 6\text{Br}^{-} + \text{N}_2 + 8\text{H}^{+}$ and $\text{Mn}^{++} + \text{Br}_2 + 3\text{H}_2\text{O} = 2\text{Br}^{-} + \text{MnO}_2\cdot\text{H}_2\text{O} + 4\text{H}^{+}$ are quant. but the amt. of Br_2 used is in slight excess of the theoretical amt. The results are explainable by assuming intermediate formation of HBrO and that this oxidizes both NH_4^{+} and Mn^{++} more readily than does Br_2 and also decomposes slightly under the exptl. conditions used into O_2 and HBr . The more ready oxidation of NH_4 in neutral soln. in presence of acetate, by its formation of H^{+} , retards pptn. of Mn. When Mn is to be pptd. after a basic acetate sepn., it is important that no appreciable amt. of NH_4 salt be present. If present, it should be removed by evapn. with HCl-HNO_3 before pptn. of Mn.

A. R. M.

Oxidations with fluorine. I. FR. FICHTER AND K. HUMPERT. *Helvetica Chim. Acta* **6**, 640-2(1923).—Brunner (*C. A.* **15**, 481) believed that he obtained K persulfate according to $2\text{KHSO}_4 + \text{F}_2 = \text{K}_2\text{S}_2\text{O}_8 + 2\text{HF}$. This reaction was restudied as F_2 is now more available through the method of Meyer and Sandow (*C. A.* **16**, 206). When F_2 was led into cold satd. aq. soln. of KHSO_4 , the soln. gave the persulfate reactions after a few min., crystals began to appear on the walls of the crucible after some hrs., and increased to a thick layer in 10-12 hrs., the soln. then evolving O_2 copiously and contg. much HF. The crude product after drying in vacuum contained about 78% $\text{K}_2\text{S}_2\text{O}_8$; 3 recrystns. from hot water gave the salt in pure condition. It gave all persulfate reactions.

A. R. MIDDLETON

Conditions of reaction of hydrogen with sulfur. II. Catalytic effect of oxygen. III. Mechanism of the reaction of hydrogen with sulfur and its catalysis by oxygen. R. G. W. NORRISH AND E. K. RIDEAL. *J. Chem. Soc.* **123**, 1689-705(1923); cf. *C. A.* **17**, 1930.—Method and app. were those previously described. Expts. were at 265°, 285° and 340° and the O_2 content varied 0-10%. The catalytic action becomes a poisoning action with rise of temp. and increase of O_2 concn. beyond 10% at 265° and 7% at 285°. The effects were sepd. into a strong poisoning effect in the gaseous reaction between H_2 and S at all temps. and a catalytic effect on the surface reaction which becomes observable only at the lower temps. where the surface reaction is relatively more important. This surface catalytic action rises to a max. with increase of O_2 (4% at 285°, 6% at 265°) then decreases and finally becomes a poisoning reaction. SO_2 is formed at a rate directly proportional to O_2 concn. The effects observed are shown to be explained quantitatively by postulating a gradual preferential adsorption of O_2 by the S surface, all H_2 being displaced when O_2 concn. exceeds 10%, and ascribing to the O_2 a catalytic activity proportional to the no. of mols. adsorbed per sq. cm. of surface. It was found possible to calc., for the first time, the compn. of the adsorbed gas film

in equil. with a given gaseous atm. The crit. increment of the gaseous reaction, found to be in good agreement with Budde's (C. A. 7, 3873) value for disoc. of S_2 into atoms, should correspond to the energy required to sever two S bonds. The crit. increment of the surface reactions should correspond to breaking one S bond and is equal to that required to sublime a mol. of S_2 from the surface, which also involves breaking one bond (Pollitzer, C. A. 4, 263). The surface reaction is considered to take place in two stages: (1) adsorption of a mol. of H_2 or O_2 , involving breaking one bond and (2) removal of the H_2S mol., involving breakage of the second bond, the measured crit. increment corresponding only to the slower of these processes. By assuming a small fraction of the stable and satd. mols., S_n , of which the surface is mainly composed, to be opened by rupture of one linkage and thus polarized, the adsorption of H_2 and O_2 and the catalytic action of the latter is plausibly accounted for. Formation of H_2O was proved not to take place and this is accounted for by the much weaker polarity of S as compared with metals like Pd.

A. R. MIDDLETON

Existence of magnesium arsines. A. JOH AND R. REICH. *Compt. rend.* 177, 56-8 (1923).—To an Et_2O soln. of 9.3 g. of $EtMgBr$ at boiling temp. was slowly added 55 g. of an Et_2O soln. contg. 5.37 g. of $C_6H_5AsH_2$. Reaction was instantaneous according to $C_6H_5AsH_2 + 2C_2H_5MgBr = C_6H_5As(MgBr)_2 + 2C_2H_6$. (1580 cc. C_2H_6 ; calcd., 1580 cc.) An oily layer formed at the bottom of the flask; addn. of a little C_6H_6 restored homogeneity. The Mg arsine is very sensitive to atm. oxidation, becoming yellow, and is decompd. at once by water with regeneration of phenylarsine. The soln. of the Mg arsine avidly absorbed CO_2 with evolution of heat and formation of abundant ppt., probably the salt $C_6H_5As(CO_2MgBr)_2$. In attempts to obtain the free acid, acidulated water caused evolution of CO_2 ; pure water hydrolyzed the compd. and the acid decomposed giving $Mg(HCO_3)_2$ and phenylarsine. The esters of this unstable acid proved more stable. Et chloroformate in boiling C_6H_6 soln. reacted according to $C_6H_5As(MgBr)_2 + 2ClCO_2Et = C_6H_5As(CO_2Et)_2 + MgBr_2 + MgCl_2$. The mixt. was heated 2 hrs., cooled and treated with ice-water, the Et_2O layer dried and distd. in vacuum. From 15.4 g. of arsine and 23 g. of chloroformate 11 g. of a colorless oil with slight ethereal odor was obtained at 180-3° and 20 mm. This product is stable in air. Dctn. of As and mol. wt. by cryoscopy in C_6H_6 agreed with the formula assigned. Treatment with hot $EtOK$ regenerated $C_6H_5AsH_2$ and on acidulation CO_2 was liberated to 83% of theory. These expts. establish the existence of Mg arsine and the possibility of attaching carboxyl directly to As.

A. R. MIDDLETON

Monochloramine, NH_2Cl . W. MARCKWALD AND M. WILHE. *Ber.* 56B, 1319-25 (1923).—When 250 cc. $NaOCl$ (from 2 N $NaOH$ and the calcd. amt. of Cl_2) contg. pieces of ice, is treated with 250 cc. of N NH_4OH , very little N is evolved. If the soln. is now distd. in the vacuum of a H_2O pump at 30-40° through a spiral condenser cooled with ice until 50-60 cc. distillate has collected, the latter is found, iodometrically, to contain 10-2% NH_2Cl . This soln. soon begins, even at 0°, to evolve N_2 and NCl_3 seps. in yellow droplets; it reacts neutral, remains clear, at first, on addn. of Ag ions but, slowly in the cold, quickly on warming or acidifying, deposits $AgCl$, does not form the corresponding chloramides when shaken with $BzCl$ or $PhSO_2Cl$, at once deposits NCl_3 on addn. of a hypochlorite. The odor of NH_2Cl is intermediate between that of NH_3 and of NCl_3 . When inhaled, it produces lassitude and a persistent headache. Analysis (Cl gravimetrically or iodometrically, N by conversion into NH_3 by treatment with SO_2) gave the ratio $Cl:N = 1$. The rate of decompn. of the soln. increases very rapidly on standing, owing to the catalytic action of the HCl formed in the decompn.; by adding traces of NH_3 , the soln. can be made quite stable. Attempts to shake out the NH_2Cl with other solvents had but little success. It is only very slightly sol. in C_6H_6 , $CHCl_3$, and CCl_4 , but when the fresh aq. soln. is shaken with Et_2O , the ratio of NH_2Cl found in equal vols. of the H_2O and Et_2O layers is about 1:0.97. When a 0.1 N soln. of NH_2Cl is warmed with an equal vol. of 0.25 N KOH (in the cold the reaction is not complete in 48 hrs.), the NH_2Cl decomp. smoothly according to the equation given by Raschig: $3NH_2Cl + 3KOH = NH_3 + N_2 + 3KCl + 3H_2O$; with 4 N KOH , however, it also decomp. to some extent (12.5%) according to the equation $3NH_2Cl + 3KOH = 3NH_3 + 2KCl + KClO_3$. In cold H_2O in the presence of $NaOAc$ to remove the H ions as fast as they are formed and of Pt sponge to catalyze the reaction, which otherwise requires several days for its completion, the decompn. follows the equation $3NH_2Cl = NH_3 + 2HCl + N_2$. Attempts to obtain a more concd. soln. of NH_2Cl than the above 10-2% distillate by repeated fractional distn. *in vacuo* resulted in violent explosions, doubtless owing to the formation of NCl_3 . When the vapors from the original $NaOCl-NH_3$ mixt. are drawn *in vacuo* through $CaCl_2$ into a cold receiver there seps. in the latter a red-brown liquid changing at room temp. to a yellow-brown gas (Cl_2O);

this can be explained by assuming the existence of an equil., $\text{NH}_2\text{Cl} + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{HOCl}$, which, as the NH_3 is absorbed by the CaCl_2 , is finally shifted completely to the right; similarly, with soda-lime instead of CaCl_2 as the dehydrating agent, only NH_3 collects in the receiver, it being the HOCl in this case which is removed from the field of action. With dry KOH , however, anhyd. NH_2Cl is obtained as an oil solidifying to a glass or, generally, crystals, m. -66° (after being freed from NH_3 at -60°), decomps. suddenly at about -50° with copious evolution of N and Cl and formation of NH_4Cl and NCl_3 . To obtain a soln. sufficiently dil. for analysis at room temp., it was distd. as above into a weighed amt. of alc. in liquid air and the receiver transferred to an $\text{Et}_2\text{O}-\text{CO}_2$ bath, whereupon the alc. melted and dissolved the NH_2Cl ; the results (Cl and NH_3) confirmed the formula NH_2Cl , which thus far has been purely hypothetical.

C. A. R.

A new method of formation of cyanates. W. MARCKWALD AND M. WILLE. *Ber.* 56B, 1325(1923).—Equiv. amts. of Javelle water and KCN soln. react quite smoothly, with evolution of much heat, according to the equation $\text{CN}^- + \text{ClO}^- = \text{CNO}^- + \text{Cl}^-$. After standing a short time, almost all the hypochlorite has disappeared. The reaction may be used for a lecture demonstration of the synthesis of urea from KCN : 100 cc. of KOCN prepd. from 2 N KOH and the calcd. amt. of Cl is treated without cooling with 50 cc. of 2 N KCN , heated to boiling, treated with 50 cc. of 2 N NH_4Cl , evapd. to about 0.5 its vol. and treated with much concd. HNO_3 , whereupon urea nitrate crystals abundantly.

C. A. R.

Action of soap on lead arsenates (PINCKNEY) 15. The brittleness of metallic compounds (TANMANN, DAHL) 9. Systematic affinity principle (BILTZ, *et al.*) 2. Presence of Ba and Sr in natural brines (FRANCIS) 8.

ROSCOE, H. E. and SCHORLEMMER, C.: *A Treatise on Chemistry*. Vol. II. **The Metals**. Pts. I and II. 6th Ed. Revised by B. Mouat Jones, *et al.* New York and London: Macmillan & Co., Ltd. 1565 pp. \$15. (50s.) Reviewed in *Chemistry and Industry* 42, 777 and *Chem. Trade J.* 73, 167(1923).

7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

Review of analytical chemistry (for 1922). A. KLING AND A. LASSIHR. *Chimie et industrie* 10, 30-48, 221-44(1923); cf. *C. A.* 16, 1542. A. PAPINEAU-COUTURE

A new indicator for acidimetry. A. REISENLEITNER. *Chem.-Ztg.* 47, 689(1923).—Extract the red petals of wild carrot (*Daucus carota*) with hot alc. and carefully neutralize with 0.1 N NaOH . A deep-red soln. with green fluorescence is obtained which may be used to replace methyl orange indicator soln. A wine-red color is obtained with acids and a deep green color with bases.

W. T. HALL

Reagents. G. C. SPENCER. *J. Assoc. Official Agr. Chem.* 7, 37-9(1923).—Of 183 lots tested only 8 were rejected. Shipment of CHCl_3 in Sn containers has led to serious difficulties.

W. T. H.

Substitution of ferric chloride for iodine in volumetric analysis. K. JELLINEK AND L. WINOGRADOFF. *Z. anorg. allgem. Chem.* 129, 15-32; *Z. angew. Chem.* 36, 440-3(1923).— FeCl_3 can be substituted for I and FeCl_3 for KI in many of the reactions of iodimetry, using as fundamental reaction: $2\text{Fe}^{+++} + 2\text{S}_2\text{O}_3^{--} = \text{S}_4\text{O}_6^{--} + 2\text{Fe}^{++}$. The end point can be detd. (1) by the decoloration of methylene blue by $\text{S}_2\text{O}_3^{--}$ after all the Fe^{+++} has been reduced, (2) by the change of blue to red when methylene blue and a little fuchsin is present, (3) by the use of an enol such as salicylic acid which gives a reddish brown color with Fe^{+++} and the color fades when all Fe^{+++} is reduced, (4) the disappearance of the yellow color of FeCl_3 , (5) by the fact that a red color is first obtained when $\text{S}_2\text{O}_3^{--}$ is added to a soln. contg. Fe^{+++} but no transitory red color is obtained after all the Fe^{+++} has been reduced. The reaction between $\text{S}_2\text{O}_3^{--}$ and Fe^{+++} takes place best in an atm. of CO_2 , in a soln. of low acidity and at a temp. of $45-60^\circ$. As standard solns., 0.1 N FeCl_3 contg. 0.2% HCl and 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ contg. 0.1% Na_2CO_3 are recommended. To titrate the two solns. against one another, take 20 cc. of FeCl_3 , dil. to 100 cc., add a little NaHCO_3 and HCl to give an atm. of CO_2 , heat to $45-60^\circ$ and titrate with $\text{Na}_2\text{S}_2\text{O}_3$ until an end point is obtained by any of the above methods, preferably (2), using 5 drops of 0.5% aq. methylene blue soln. and 3 drops of satd. aq. fuchsin soln. For titrating the hot solns. it is well to use a Mohr buret delivering

through a fairly long horizontal side arm, to avoid heating the contents of the buret.

Detn. of $KMnO_4$.—Take about 100 cc. of an acid, 5% $FeCl_3$ soln. in a 300 cc. Erlenmeyer flask. Add 1–2 g. of pure Fe and boil until decolorized. Filter off the excess Fe into a flask contg. CO_2 . To this add a measured vol. of $KMnO_4$ soln. from a buret or pipet. The reaction between the $KMnO_4$ and $FeCl_3$ takes place immediately. Neutralize the excess acid with soda soln. until a slight turbidity results, add 1 cc. of 6 N HCl and titrate with $Na_2S_2O_3$ at 45–60°. **Detn. of $KClO_4$.**—Proceed in the same way as with $KMnO_4$ but to effect complete reduction of the chlorate, slowly raise the temp. to the b. p. and boil 1 min. in CO_2 . Then titrate the Fe^{++} . **Detn. of MnO_2 in pyrolusite.**—Treat 0.15 g. of powdered ore in a 300 cc. Erlenmeyer flask with a strongly acid $FeCl_3$ soln. and boil in CO_2 atm. until all the black oxide has dissolved. Adjust the acidity and titrate the $FeCl_3$ with $Na_2S_2O_3$. **Detn. of KNO_3 .**—Proceed similarly but heat, while passing CO_2 through the soln., until all brown fumes have been expelled. **Detn. of Sn in white metal.**—Treat 1 g. of borings with 15 cc. of concd. HCl and about 30 cc. of 5% $FeCl_3$ soln. Heat gently but do not boil. Add 5 g. Fe powder to ppt. Cu and Sb. Filter and wash with hot water into a flask contg. a little $NaHCO_3$. Titrate the hot $SnCl_2$ soln. with $FeCl_3$ soln. using methylene blue as indicator. Good results are obtained if the soln. is standardized in the same way against pure Sn. **Detn. of Na_2S .** To the $FeCl_3$ soln. in an Erlenmeyer flask add 5 cc. of concd. HCl, heat to 40–50° and rapidly add the Na_2S soln. from a buret. Stopper the flask and allow to stand over night. Then filter off the S and titrate the excess $FeCl_3$ with $Na_2S_2O_3$ soln. Good results were obtained by all of these methods, which are analogous to the usual reactions of iodimetry, but poor results were obtained in attempting to titrate H_2O_2 or sulfite solns.

Electrometric titration of acids and bases with an antimony indicator electrode. ALFRED UHL and WILHELM KESTRANEK. *Monatsh.* **44**, 29–34 (1923). In the electrometric titration of acids, using an indicator electrode of Sb without using O_2 , a sharp potential difference is obtained in 0.1 N soln. at the neutralization point. This is of sufficient magnitude so that the final const. value of the potentials need not be waited for after each successive addn. of the titrating fluid. Titration with a reversible electrode is also possible. Chlorides have no effect in any case and NH_4 salts have no effect with strong acids.

Introduction of hydrogen sulfide. F. HAHN. *Chem.-Ztg.* **47**, 641 (1923). H. has long used the method described by Remy (*C. A.* **17**, 2977), but it is better to pass the H_2S into a cold soln. quite strongly acid with HCl. The As is pptd. at once. If the soln. is very strongly acid nothing but As is pptd., or at most only Hg. If the soln. is diluted and the passage of H_2S continued, the metals will be pptd. successively, so that with a little practice a good guess at the compn. of the substance may be made from the nature of the ppt.

Titration of iodides according to Winkler. I. M. KOLTHOFF. *Pharm. Weekblad* **60**, 841–5 (1923).—Winkler's method, which consists in oxidizing iodides to iodates by means of Cl_2 , boiling out the excess of Cl_2 , and titrating the HIO_3 with KI , is subject to certain limitations. If bromides are present, the magnitude of the error is proportional to the H^+ concn. at which the oxidation is performed. The use of $AcOH$ is inadvisable because of traces of CH_3O_2 which it may contain. By using chloride of lime in place of Cl_2 for oxidation, and succinic acid for acidifying, iodides may be detd. accurately in the presence of 10 parts of bromide. If Fe is present the oxidation should be performed in the presence of H_3PO_4 . The modified method is of course not applicable in the presence of org. matter such as sugar, *e. g.*, in sirup of $FeCl_2$.

Detection of iodate ions in the presence of chlorate, bromate, dichromate, nitrate and other anions. M. DIMITROFF. *Z. anal. Chem.* **52**, 452–3 (1923).— $Na_2S_2O_3$, even at low concns., reduces iodate in slightly acid soln. to iodide but its action upon bromate and chlorate is much weaker. The reaction can be applied to a test for iodate in 2 ways: (a) To 4–5 cc. of the soln. in a test-tube, add 2–3 drops of starch soln., 5–6 drops of dil. H_2SO_4 , and 1 drop of 0.5% $Na_2S_2O_3$ soln. If iodate is present, an intense blue coloration results. (b) To 4–5 cc. of soln. add dil. H_2SO_4 till slightly acid and a little starch soln. From a pipet, cover the mixt. with 1–2 cc. of 0.5% $Na_2S_2O_3$ soln. A blue ring appears at the junction of the 2 solns. if IO_3^- is present. By method (a) it is possible to detect 0.05 mg. of KIO_3 in the presence of 0.1 g. of $KClO_3$ or $KBrO_3$ in 10 cc. of aq. soln. By method (b) it is possible to detect iodate in the presence of ClO_4^- , Cl^- , PO_4^{--} , ClO^- , Fe^{+++} , Cu^{++} , $Cr_2O_7^{--}$, MnO_4^- , etc.

New method for detecting chlorate and bromate in mixtures of halogenates, the qualitative investigation of such mixtures and the utilization of the method for the detection of bromate in chlorates and iodates. M. DIMITROFF. *Z. anal. Chem.* **62**,

453-5(1923).—*Detection of chlorate in the presence of bromate and iodate.*—Place 40-50 cc. of 2 *N* H₂SO₄ in a beaker, heat to boiling, add 2-3 small pieces of Zn and then 5-6 cc. of the soln. to be tested. Boil till the iodate is completely reduced and the I₂ all expelled, as shown by testing a few cc. of the soln. for iodate with Na₂S₂O₃ soln. Remove the excess Zn, boil a little longer to be sure that there is no more free halogen in the soln. and test for chloride with Ag⁺. *Detection of bromate in the presence of chlorate and iodate.*—To 5-6 cc. of the soln. in a test-tube add an equal vol. of 18 *N* H₂SO₄, cool and add 1 cc. of CHCl₃. Then add 0.4-0.5% alc. I soln. and shake 10-15 times after the addn. of each drop. If bromate is present the reddish color of the CHCl₃ soln. disappears owing to the formation of IO₃⁻ by the action of I upon BrO₃⁻ and soon the yellow color due to free Br appears in the CHCl₃ soln. In the absence of iodate the free I reacts slowly with chlorate if it is present and the CHCl₃ is decolorized very slowly. If chlorate is absent, the I color of CHCl₃ can be decolorized with Cl₂ water and there will be no yellow shown by the CHClO₃ if bromate is absent. *Purity test for chlorates and iodates.*—Prepare a concd. aq. soln. and test for bromate as just described. If 0.04% of bromate is present, a positive test will be obtained. *Test for each halogenate in a mixt.*—Test a portion for iodate as follows: Make 2-3 cc. of the aq. soln. acid with H₂SO₄, add starch and shake. Cover with 1-2 cc. of 0.5% Na₂S₂O₃ soln.; a blue ring at the zone of contact shows iodate to be present. Test other portions for bromate and chlorate as described above. W. T. H.

Detection of chlorine and bromine in the presence of closely related ions. M. DIMITROFF. *Z. anal. Chem.* 62, 451-2(1923).—*Detection of Cl⁻ in the presence of Br⁻, I⁻, CN⁻, CNS⁻ and other anions.*—To the concd. soln. add 4-5% KMnO₄ or 10% CrO₃ and expel the liberated halogen by a stream of air into 3-4 cc. of 0.07% KBr soln. In this way the evolved Cl₂ will change all or a part of the KBr to KCl. Evap. the absorbent in an air stream to a vol. of about 1 cc., cool and add 6 cc. of 2% KBrO₃ soln. and 6 cc. of 5 *N* H₂SO₄. To remove Br₂ heat the soln. in an air stream for 15 mins. Test to see if any more free Br is present by passing the air stream into a soln. of KI and starch. Then, when all of the Br is removed, test for Cl⁻ with a drop of 3% AgNO₃ soln. In this way, 0.025 mg. of NaCl can be detected in the presence of 0.4 g. of KBr. The test succeeds even with an insol. or undissociated halide. *Detection of Br⁻ in the presence of I⁻, CNS⁻ and other ions.*—Oxidize in the same way but substitute KI for KBr in the absorbent. Test for Br⁻ with Cl₂ water and CHCl₃ in the usual way. In this way 0.5 mg. of KBr can be detected in 1 g. of KI. W. T. HALL

Rapid method for determination of carbon. RICHARD RIMBACH. *Forging and Heat Treating* 9, No. 6(1923); *Bull. Cleveland Sci. Tech. Inst.* 2, 570(1923).—Details are given for the rapid detn. of C in Fe and steel by direct combustion. W. T. H.

The estimation of carbon dioxide. F. H. CAMPBELL. *Chem. Eng. Mining Rev.* 15, 372-3(1923).—By the use of ascarite as absorbent in the usual train, fairly concordant results were obtained. The most satisfactory results were obtained, however, in the analysis of white lead by introducing 3 g. of sample into a 250 cc. flask fitted with a rubber stopper carrying a drop funnel through which acid can be added or CO₂-free air introduced and a delivery tube leading to a 500 cc. flask contg. 100 cc. of satd. Ba(OH)₂ soln. and a few drops of phenolphthalein soln. After the app. is ready apply gentle suction and add 80 cc. of 6 *N* HCl. After the reaction slackens heat the soln. to boiling and expel all the CO₂ with the aid of CO₂-free air. Finally neutralize with HCl until the phenolphthalein is decolorized and titrate the BaCO₃ ppt. with standardized acid using methyl orange as indicator. W. T. HALL

The use of mercurous iodide in the determination of nitrogen. E. S. RICHARDS. *Chem. Eng. Mining Rev.* 15, 369(1923); cf. Sborowsky, *C. A.* 16, 4156.—A great saving of time has been obtained by the use of 0.25 g. of Hg₂I₂ for the Kjeldahl digestion of substances like leather or coal. W. T. H.

The determination of nitrogen compounds in impure sulfuric acid. O. NYDEGGER. *Bull. fed. ind. chim. Belg.* 2, 367-8(1923).—N. finds that the nitrometer method is unreliable for the analysis of H₂SO₄ from the Glover tower. It is better to drive over the NO, formed by reduction with FeSO₄, by a current of air, to absorb it in pure H₂SO₄, and to titrate with KMnO₄ soln. R. BEUTNER

Titrimetric estimation of mercuric aminochloride. D. KOESZEGI. *Pharm. Ztg.* 68, 577-8(1923).—Dissolve 2.520 g. (0.02 g. equiv.) of the sample in an excess (50 cc.) of 0.5 *N* HCl (incomplete soln. indicates contamination with Hg₂Cl₂, from which the liquid should be filtered). After cooling, titrate excess of HCl with 0.5 *N* NaOH with methyl orange as indicator. During this operation a ppt. forms which dissolves on shaking as long as any excess of HCl is present. In case the sample is pure, 40 cc. of 0.5 *N* HCl are required for 2.520 g. HgCINHg. W. O. E.

The effect of silicic acid hydrosol upon the titration of ferrous salt in hydrochloric acid solution. L. BRANDT. *Z. anal. Chem.* 62, 417-50(1923).—R. Schwartz has published during the last 3 yrs. several papers claiming that it was advantageous in the Zimmermann-Reinhardt method for titrating Fe with KMnO_4 to add a little water glass soln. assuming that the error caused by the oxidation of HCl, and not absolutely prevented by the addition of MnSO_4 soln., was prevented by colloidal silicic acid. In this paper about 300 careful expts. in dil. solns. are described which indicate that there is no effect of the colloid along the lines suggested by S. The addition of water glass soln. serves partly to neutralize the acid, and the same effect can be accomplished by adding Na_2CO_3 , and it is also likely to contain traces of oxidizable material. Its favorable effect appears to be mythical. W. T. HALL

Determination of total solids in brines. N. N. EFREMOV. *J. Russ. Phys. Chem. Soc.* 51, 399-415(1919).—Direct evapn. is likely to cause trouble owing to hydrolysis and hygroscopicity. Make a rough estn. of the solid content by detg. the d. If this is less than 1.26 assume that the wt. of dry solids, $Q = (d-1)120$; if greater than 1.26 assume $Q = (d-1)110$. Add 2.0-2.5 times as much anhyd. Na_2CO_3 dissolved in hot water, evap. to dryness, heat at 105° for 1 hr. and then at 150° for 5-6 hrs. M. G. KORSUNSKY

Determination of zinc and copper in gelatin and glue. R. HERTWIG. *J. Assoc. Official Agr. Chem.* 7, 41-3(1923).—Place 20 g. in a small dish, cover with a small filter paper and heat carefully till charred. Leach the charred mass with water, filter and save the filtrate. Ignite the filter and its contents in an elec. muffle, raising the temp. gradually. Digest the ash with 25 cc. of 6 N HCl, filter and add the filtrate and washings to that obtained by the first leaching. Add methyl orange and NH_3 aq. till neutral. Then add enough excess to form the sol. NH_3 complexes with Zn and Cu. Heat to 80° , filter and wash with 3% NH_4Cl soln. contg. about the same quantity of NH_3 as the original soln. Neutralize the filtrate with HCl and add 5 cc. concd. acid in excess for each 100 cc. of soln. Ppt. CuS with H_2S and det. the Cu by the official volumetric method. Make the filtrate from the CuS slightly ammoniacal, neutralize with 2.5 N HCl and add 1 cc. in excess. Ppt. ZnS , filter, wash with 2% NH_4NO_3 soln. which is satd. with H_2S , ignite the ppt. in porcelain and weigh as ZnO . W. T. HALL

The volumetric determination of uranyl compounds. G. JANDER AND K. REEH. *Z. anorg. allgem. Chem.* 129, 293-301(1923).—In attempting to reduce uranyl salt with Zn the usual difficulties were encountered but when a German Al coin was used and the reduced soln. titrated with KMnO_4 excellent results were obtained. To 100 cc. of soln. contg. about 0.2 g. of U, in a 400 cc. Erlenmeyer flask, add 20 cc. of concd. H_2SO_4 and heat just to boiling. Close the flask with a rubber stopper fitted with an improved Bunsen valve and a rod to which is attached a glass basket of 10-15 cc. capacity. This basket can be made from the bottom of a test-tube perforated with many holes. Place several pieces of Al in the basket and reduce the hot soln. out of contact with the air. After an hr. or longer, raise the stopper, add a little NaHCO_3 soln., wash off the glass basket and its contents and titrate with 0.1 N KMnO_4 . The reactions involved are as follows: $3\text{UO}_2^{++} + 2\text{Al} + 12\text{H}^+ \longrightarrow 3\text{U}^{+++} + 2\text{Al}^{+++} + 6\text{H}_2\text{O}$, $5\text{U}^{+++} + 2\text{MnO}_4^- + 2\text{H}_2\text{O} \longrightarrow 2\text{Mn}^{++} + 5\text{UO}_2^{++} + 4\text{H}^+$. W. T. HALL

The volumetric determination of phosphoric acid with the aid of uranium acetate solution. G. JANDER AND K. REEH. *Z. anorg. allgem. Chem.* 129, 302-5(1923).—To the hot, neutral soln. contg. NH_4OAc , add a slight excess of $\text{UO}_2(\text{OAc})_2$ soln. and ppt. $\text{UO}_2\text{NH}_4\text{PO}_4$. Filter and wash with hot 2% AcONH_4 soln. It is convenient to use a membrane filter. Transfer the ppt. to a 400 cc. Erlenmeyer flask, dissolve it in 120 cc. of 6 N H_2SO_4 , reduce and titrate as described in the preceding abstract. W. T. HALL

Determination of sulfur in oils by combustion in a closed vessel at ordinary pressure. ENRIQUE HAUSER. *Chimie et industrie Special No.*, 231-2(May, 1923).—The oil is absorbed in cotton and placed in a special burner consisting of two concentric quartz, alundum, or preferably Pt, vessels, the smaller of which is perforated near the bottom, and is burned in a 12 l. bottle filled with O_2 which is immersed in water during combustion. The SO_2 is absorbed in a 0.5% Na_2O_2 soln. and detd. as BaSO_4 . A. PAPINEAU-COUTURE

Progress in the field of metal analysis in 1922. TH. DÖRING. *Chem.-Ztg.* 47, 605-7, 622-3, 630-1, 650-2, 660-8, 675-6, 689-90, 693-5(1923). E. H.

Sampling custom ores. W. A. LINFESTY. *Eng. Mining J. Press* 116, 281-3 (1923).—A partial flow sheet is given showing how ores were sampled at the Tom Reed Mill in Arizona before the introduction of an automatic sampler. W. T. H.

The separation and determination of potassium and sodium. A perchlorate pre-

precipitation process using normal butyl alcohol. G. F. SMITH. *J. Am. Chem. Soc.* **45**, 2072-80(1923).—Instead of adding EtOH to the fumed mixt. of KClO_4 , NaClO_4 , and HClO_4 , add 2-3 cc. of water and dissolve the solids by heating. To the warm soln. slowly add 65-100 cc. of butylalc. contg. 0.5-1% HClO_4 . Boil for 30 secs., cool, filter and wash with butyl alc. Dry at 150-250° and weigh the KClO_4 . Evap. the filtrate to fumes of HClO_4 and keep at this temp. till the org. matter is all oxidized, then add 0.5 cc. of concd. H_2SO_4 , evap. and weigh the Na_2SO_4 . W. T. H.

Electrometric titration of iodate, bromate, chlorate and ferricyanide with titanous sulfate. W. S. HENDRIXSON. *J. Am. Chem. Soc.* **45**, 2013-7(1923).—Iodate in 1-2 *N* H_2SO_4 soln. can be titrated at room temp. with 0.05 *N* $\text{Ti}_2(\text{SO}_4)_3$ soln. and 2 electrometric end points are obtained. The first corresponds to the reduction of iodate to I_2 and the second to I^- . The former is preferred with iodate. Bromate in 0.5 *N* HCl or H_2SO_4 can be titrated similarly but the second end point is sharpest. Chlorate behaves similarly in 1-4 *N* HCl or H_2SO_4 soln. Ferricyanide can be titrated as easily as any other compd. contg. tervalent Fe. W. T. H.

The electrometric determination of manganese. E. MÜLLER AND O. WAHLE. *Z. anorg. allgem. Chem.* **129**, 33-40(1923).—It is possible to carry out the Volhard titration of Mn^{++} with MnO_4^- and det. the end point electrometrically. The results agreed with those obtained by the ordinary method, showing the necessity of having Zn^{++} or KNO_3 present and being slightly lower than the theoretical values. Near the end point it required about 7 mins. to establish the true e. m. f. break. A somewhat easier end point was obtained in HF solns. in which case the Mn^{++} was oxidized to Mn^{+++} and the MnO_4^- reduced to Mn^+ . The best results were obtained in a vol. of 100 cc. in a soln. 0.4 *N* with H_2SO_4 and contg. 8 g. of KF. It is hoped that the method can be applied to the titration of Fe^{++} and Mn^{++} in the presence of one another. W. T. HALL

A new reaction for rhodium, and a colorimetric method for its determination. V. N. IVANOV. *J. Russ. Phys. Chem. Soc.* **50**, I, 460-2(1918).—The qual. test is carried out as follows: To 1 cc. of a mineral acid soln. of a salt of Rh 1 cc. of a 40% SnCl_2 soln. in 30% HCl is added in a small test-tube. The mixt. is heated to boiling and cooled. In the presence of small amts. of Rh the mixt. becomes brown during heating, and on cooling a beautiful raspberry-red color develops. In the presence of an excess of Rh this color change is slow and may take an hr. before the appearance of the red., but with only traces of Rh present the color change is very rapid. The reaction is claimed to be sensitive to 0.0006 mg. Rh in 1 cc. In the presence of an excess of other metals the test is facilitated by previous fusion of the material with KHSO_4 , leaching with H_2O , filtration and evaporation of the filtrate to 1 cc. Since the final red color of the reaction is stable a series of tubes contg. increasing amts. of a pure Rh salt is prepared as above and is used as a colorimetric scale for quant. detns. W. A. PERLZWEIG

The determination of antimony and the separation of this element from tin. P. WENGER AND G. PARAUD. *Ann. chim. anal. chim. appl.* **5**, 230-2(1923).—The results of a series of comparative expts. indicate that the detn. of Sb as Na_3SbO_7 by the method of Rose gives results much below the truth; the method of Henz is reliable but tedious; the method of Wortmann and Metzl is satisfactory; the method of Bunsen and Baubigny gives slightly low values; and Classen's method of pptg. Sb with Sn or Cd is very satisfactory. For sepg. Sn and Sb, the Clarke method is accurate but tedious; the method of Rose should be rejected but Tomula's recent modification of the Rose method is satisfactory. W. T. H.

Halphen number disk. A practical apparatus for the calculation and rapid application of the Halphen rule. ANON. *Ann. chim. anal. chim. appl.* **5**, 232-3(1923).—The firm of Dujardin-Salleron of Paris has a circular scale which is convenient for use in detg. the alc. content and Halphen no. of wines. W. T. H.

The so-called pyrrole reaction. E. S. KHOTINSKI. *J. Russ. Phys. Chem. Soc.* **49**, I, 149-53(1917).—A review of the literature and some original exptl. data lead K. to conclude that the Runge reaction for pyrrole with a pine splinter moistened with HCl yielding a red coloration is sp. neither for pyrrole nor for pine wood. Various polyhydric phenols react similarly to pyrrole, while PhOH itself gives a blue color. The substance in the wood responsible for the reaction is *coniferin* or its derivs. (e. g., vanillin), and the reaction was obtained with a no. of woods of different species and notably with asparagus pulp which is rich in *coniferin*. W. A. PERLZWEIG

Assay of methanol. Frequency of impurities reacting with iodized potassium iodide and with potassium permanganate. F. RICHARD. *J. pharm. chim.* **27**, 456-81(1923).—Present com. MeOH , some samples even being labeled 99.5% pure, contained

4.4 to 37.2 g. of ketone per l., and several cc. instead of 1 drop of 0.1 *N* KMnO_4 were consumed.

Determination of β -naphthol in α -naphthol and of α -naphthol in β -naphthol. S. WALDBOTT
J. PROCHAZKA. *Ind. Eng. Chem.* 15, 944-5 (1923).—Dissolve 0.36 g. α -naphthol (*A*) in 30-40 cc. alc. At 5° or lower, slowly add β -nitrodiazobenzene (100 cc. = 1 g. of nitrite). If *A* is pure, 17.25 cc. will be required. If β -naphthol (*B*) is present para-red will be formed after all of *A* has reacted. From the vol. required to get a red spot test, the percentage purity of *A* can be computed. To detect *A* in *B*, dissolve 1.44 g. of *B* in 50 cc. alc., add 3 cc. of β -nitrodiazobenzene and 0.03 g. nitrite. If the percentage of *A* is less than 0.5 all of *A* and some of *B* will be pptd. After 30 mins., dil., filter and wash the ppt. Boil with 0.1 *N* NaOH and match the color with that produced similarly with known amts. of *A*.

W. T. HALL

Volumetric estimation of NH_3 and carbamide N by the hypobromite method (TILMANS, KRÜGER) 1. Use of H_2O_2 in the estimation of N (HEUSS) 16. Vanadic acid iodates, periodates and a few phosphates with a note on the alkalimetric determination of vanadic acid (ROSENHEIM, YANG) 6.

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MÜLLER, E.: **Die Elektrometrische Massanalyse.** Dresden and Leipzig: Theodor Leipzig. 159 pp. 3s. 5d.

SMITH, HERBERT O.: **An Outline for Qualitative Analysis.** New York: D. Van Nostrand Co. 4 pp. 10 cents.

8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND EDW. F. HOLDEN

Finnemanite, a new lead arsenite from Långban. G. AMINOFF. *Geol. For. Forh.* 45, 160-3 (1923).—Finnemanite, a new arsenite of Pb from Långban, is described. It occurs in cracks in a granular iron pyrite and is embedded in a crust of yellowish gray, scaly mineral of unknown compn. Crystals are hexagonal prisms, 2 cm. in length with forms (10 $\bar{1}$ 0), (10 $\bar{1}$ 1) and (0001). $c = 0.6880$. Optically —; luster is high; $\omega = 2.2949$; $\epsilon = 2.3847$; cleavage parallel to (10 $\bar{1}$ 1); hardness = 2-3; sp. gr. 7.08 (by pycnometer detn.), 7.265 (by weighing in air and in benzene). Its compn. is $\text{PbO } 78.83$, As_2O_3 20.54, Sb_2O_3 trace, FeO trace, $\text{CaO } 0.39$, $\text{Na}_2\text{O } 0.24$, $\text{K}_2\text{O } 0.44$, $\text{Cl } 2.42$, sum 100.86, —O = Cl 0.55, cor. sum 100.31%, indicating $\text{Pb}_2\text{Cl}(\text{AsO}_3)_2$ or $3\text{Pb}_2(\text{AsO}_3)_2 + \text{PbCl}_2$.

W. SEGERBLOM

Some effects of heat on the properties of minerals. J. T. LONSDALE. *Am. Mineral.* 8, 141-7 (1923).—The effects of a fire on 50 minerals, from a collection housed in the burned building, are described. Most of the changes suffered by the minerals were those to be expected. Fluorite, cyanite, prehnite, lepidolite and turquoise lost their color, while in some other cases the color was changed. Some Cu and Pb minerals were decomposed with the liberation of volatile constituents and the metal. E. F. H.

Spectrophotoelectrical sensitivity of bournonite and pyrrargyrite. W. W. COBLENTZ AND J. F. ECKFORD. *Bur. of Standards, Sci. Paper No. 451*, 353-72 (1922).—"The present paper, considered in connection with previously published data on proustite, represents a study of the effect of chem. constitution upon spectrophotoelectrical sensitivity. Exptl. data are given on the effect of temp. and of the intensity of radiation stimulus upon the spectrophotoelectrical sensitivity of bournonite, $3(\text{Cu}_2\text{Pb})\text{S}_3\text{AsS}_4$, and of pyrrargyrite, Ag_3SbS_4 . The observations on the latter are compared with similar data previously published on proustite, Ag_3AsS_4 . The results obtained are in agreement with the previously formulated (cf. *C. A.* 15, 3788) general characteristics of spectrophotoelectrical conduction in solids." In a general way the properties of photoelectrical reaction spectra, with reference to temp. and intensity of radiation stimulus, are analogous to properties of absorption spectra as affected by chem. constitution, from which it appears that perhaps ultimately the 2 phenomena may be traced to a common source within the mol.

L. W. RIGGS

Cubanite: identity with chalmersite; magnetic properties. H. E. MERWIN, R. H. LOMBARD AND E. T. ALLEN. *Am. Mineral.* **8**, 135-8(1923).—The published descriptions of cubanite from Cuba and Sweden agree with the properties of chalmersite from Brazil and Alaska, and new data confirm the identity. Cubanite is the older name. The mineral is unique among known strongly magnetic substances in having only one axis (*a*) of high magnetic susceptibility. E. F. H.

Cobaltiferous gahnite from Maryland. E. V. SHANNON. *Am. Mineral.* **8**, 147-8 (1923).—Deep blue gahnite was found at several old Cu mines in Carroll Co., Md. It occurs as small octahedral crystals and granular masses, in quartz veins in schist. The color is due to Co, as shown by the analysis of material from the Mintz Hill mine: insol. 1.05, SiO₂ 1.50, Al₂O₃ 54.50, FeO 4.86, MgO 0.42, ZnO 34.48, CoO 1.48, CuO 0.14, MnO 0.26, sum 99.14%. A faint absorption band was observed at 550 μ ; $n = 1.788-1.792$. E. F. H.

The chemical formula of uraninite. A. SCHÖPF. *Bull. soc. chim. Belg.* **32**, 275-81 (1923).—Uraninite was treated with concd. HCl which dissolved most of the impurities, especially becquerelite (UO₃·2H₂O), leaving a rather pure uraninite as a black insol. powder. This was analyzed and found to contain: UO₃ 52.47, UO₂ 37.12%, apart from SiO₂ 1.2, PbO 6.9, Fe₂O₃ 0.5 and Se 0.7%—which constituents are looked upon as impurities. From these figures the chem. formula (UO₂)₂(UO₃)₂ is derived for this uraninite. R. BEUTNER

Euhedral magnesite crystals from San Jose, Calif. A. F. ROGERS. *Am. Mineral.* **8**, 138-40(1923).—The first described U. S. occurrence of distinct crystals of magnesite is at the abandoned San Juan quicksilver mine near San Jose. Veins of magnesite occur in an altered serpentinite, the crystals being found in cavities. They are 1 by 7-8 mm. and of scalenohedral habit, with these forms: *v* (21 $\bar{3}$ 1), *c* (0001), *a* (11 $\bar{2}$ 0), and *f* (02 $\bar{2}$ 1). An analysis by K. S. Boynton of cleavable vein material gave: MgO 42.26, CaO 1.74, FeO 1.27, CO₂ 50.48, H₂O none, insol. none, sum 99.75%. Its $\omega = 1.704$, and sp. gr. = 3.05. E. F. H.

Contributions to Mexican mineralogy. Dumortierite in the pegmatites of the Guadalucazar range. E. WITTICH AND J. KRATZERT. *Mem. rev. Soc. cient. "Antonio Alzate"* **1922**, 651-5; cf. *C. A.* **17**, 372.—The occurrence of dumortierite was noted in the Realejo granite. The color was an intense blue and the crystals were slender, 25 μ or less. The quartzite matrix also contained fine inclusions of muscovite, topaz, and in smaller quantities magnetite and hematite. A possible explanation of the mineralogical history is given. **Volcanic ashes in the Guadalucazar placers.** *Ibid.* 655-61.—W. and K. establish relationship between these ashes and the rhyolites of San Luis Potosi, fixing the geologic age thus as probably Miocene. *Beryl* was also found in the pegmatites associated with quartz, microscopic topaz, and unidentified cryst. masses, thought to be rare earths. O. B. HELFRICH

Baralite of Bas-Vallon. J. ORCEL. *Compt. rend.* **177**, 271-3(1923).—The sample studied was of remarkable purity, consisting of a compact chlorite of fine scales, d. = 3.20, resembling certain ripidolites of the Alps. Its birefringence is a little less than that of quartz. The optic axial angle is slight; the mineral is optically negative and pleochroic. Analysis gave: SiO₂ 21.71, TiO₂ 0.08, Al₂O₃ 21.35, Fe₂O₃ 0.82, FeO 43.01, MnO 0.05, MgO 2.33, CaO 0.16, alkalis 0.35, H₂O at 107° 0.11, H₂O at 485° 9.03, H₂O at 735° 1.07, sum 100.07%; formula 2SiO₂·Al₂O₃·3FeO·3H₂O. Baralite therefore falls in the series of prochlorites. It resembles the chamossites but an analysis of a pure sample of the latter would be necessary to prove their identity. L. W. RIGGS

Porcupine ore deposits. L. D. HUNTOON. *Trans. Am. Inst. Mining Met. Eng.* **1272M**, 6 pp.(1923).—Gold occurs in the Porcupine area of northern Ontario. It is associated with porphyry intrusions in a schistose brecciated greenstone. Au is both visible and contained in pyrite. Since 1912 the district has produced over \$100,000,000 in Au. E. F. H.

Genesis of the Puhupuhi cinnabar deposits: a working hypothesis. W. H. CROFF. *New Zealand J. Sci. Tech.* **5**, 173-7(1923).—This geological study appears to show that the cinnabar deposits are not outcrops of deep-seated lodes, but form a surface sheet probably not exceeding 30 ft. thick. The extn. of the cinnabar calls for quarrying, not mining operations. Directions for prospecting are given. L. W. RIGGS

The lime belt of Massachusetts and parts of eastern New York and western Connecticut. T. N. DALE. U. S. Geol. Survey, *Bull.* **744**, 67 pp.(1923).—Seven quadrangles with their lime deposits are described. The *calcareous limestones* are classified as (1) those used for finishing lime, (2) those not making the best finishing lime, (3) those discarded on account of accessory minerals, and (4) those discarded on account of texture or content of Mg. The *dolomitic limestones* are classified as (1) those used

for magnesian lime, (2) those discarded on account of accessory minerals, and (3) those discarded on account of behavior under fire. Chem. analyses of 13 specimens are recorded and 13 photomicrographs of thin sections are shown. The granular and semi-granular dolomitic limestones are described, also the structure exposed in various quarries. The relations of geologic formation to cost of quarrying and to future prospecting are indicated.

L. W. RIGGS

The Italian leucite deposits: their utilization and method of working. C. MATIGNON. *Recherches et inventions* 4, 635-41, 661-71 (1923). A description of the deposits and of the various processes for working them. (See Blanc and Jourdan, C. A. 15, 725, 1785; 16, 2202, 2760, 3176, 3736; 17, 1300; Poudio, C. A. 16, 2012.)

A. PAPINEAU-COUTURE

How was petroleum formed? A. P. BJERREGAARD. *Petroleum Age* 12, No. 4, 26 (1923).—Petroleum prepd. from fish oil does not resemble natural petroleum sufficiently to warrant belief in this theory of petroleum origin. In similar manner hydrocarbons from coal are believed to have no common origin with petroleum. The theory is advanced that petroleum was more likely formed from the hydrocarbons given off by molten Fe in the hot bowels of the earth.

D. F. BROWN

Progress report on a subsurface study of the Pershing oil and gas field, Osage County, Oklahoma. U. S. Geol. Survey, *Bull.* 751B, 23-70 (1923).—The stratigraphy and structure of the field as shown by the exposed rocks and by well records are described. The relations of future production of oil and gas fields to individual well data, the geologic and other conditions are discussed.

L. W. RIGGS

Cherts and igneous rocks of the Santa Elena oil field, Ecuador. J. H. SISCLAIR AND C. P. BERKEY. *Trans. Am. Inst. Mining Met. Eng.* 1270M, 11 pp. (1923). Oil is collected from surface pits in cherts. Petrographic descriptions and photomicrographs are given of 9 chert specimens and of one of an associated diabase.

E. F. H.

The geological structure of the petroleum fields of Northern Italy. M. GIGNOUX. *Mat. grasses* 15, 6494-6 (1923).

A. PAPINEAU-COUTURE

Petrology of the Hawaiian Islands. II. Hualalai and Mauna Loa. H. S. WASHINGTON. *Am. J. Sci.* 6, 100-25 (1923); cf. C. A. 17, 2697. Mt. Hualalai attains the height of 8269 ft. and its last known eruption occurred in 1801. Analyses of 4 olivine basalts, 3 trachytes and one each of aphyric basalt, feldspar aphyric basalt and gabbro, by W. are recorded. Mauna Loa, height 13,675 ft., has had recent eruptions. Analyses of 4 aphyric andesine basalts, 3 picrite basalts, and one olivine-oligoclase basalt are recorded, also 4 analyses of ancient lavas by Bailey. In the early stages of the volcano there occurs a fairly well defined succession in time of 3 main types of lava, each extending over a considerable period. This is followed in the present period by lavas of all 3 types in irregular succession.

L. W. RIGGS

Mineralogic composition of certain marls of the Tertiary in Alsace. THIÉBAUD. *Compt. rend.* 177, 273-6 (1923); cf. C. A. 17, 46.—Five samples were analyzed. Four of these were similar in compn., the ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ being about 4.0, $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ about 2.0 except in one sample contg. heavy hydrocarbons in which this ratio was 1.56, bases/ Al_2O_3 1.70-1.76. These marls, like those of the Keuper Lorraine beds, are composed of calcite and accessory dolomite, a hydro-silico-aluminate of Fe and Mg contg. Na and K, white mica and quartz. They contain practically no clay.

L. W. RIGGS

Presence of barium and strontium in natural brines. A. G. FRANCIS. *Analyst* 48, 315-20 (1923).—Quantities of Ba and Sr each amounting sometimes to about 1 g. in 100,000 of water have been identified in English and Scottish brines, obtained in boring for oil. The method of analysis consisted in removing Fe and Al with NH_4OH , pptg. the Ba as BaSO_4 after the removal of the Sr and Ca as oxalates, conversion of the oxalates to oxides by ignition and to nitrates by treatment with HNO_3 and treatment of the anhyd. nitrates with alc. The presence of the Ba and Sr is accounted for as follows: Water charged with CO_2 falls upon igneous rocks contg. feldspar, hyalophanes and micas; some alk. earth passes into soln. as bicarbonate. The water subsequently percolates through a rock or stratum contg. zeolites or kindred minerals which retain the alk. earth like a permutite filter; then when strong brine comes in contact with the zeolite there is an exchange of alk. earth for Na. This view is supported by certain lab. expts. Complete analyses of several brines are given.

W. T. HALL

Geochemistry of the thermal lakes, North Island, N. Z., in relation to problems bearing on the acclimatized Salmonidae. W. J. PHILLIPS AND F. J. T. GRIGG. *N. Zealand J. Sci. Tech.* 5, 156-65 (1922).—The waters of 16 streams, lakes or springs were analyzed by standard methods, the dissolved O being detd. by the process of Thresh

as described by Kenwood. Each sample is discussed with reference to its potability and to its suitability as a habitat for trout or other fish. L. W. RIGGS.

Quantitative decomposition of native fluorspar by fusion with excess of Na_2CO_3 (PALIT) 6.

9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST, R. S. WILLIAMS

Physico-chemical observations of the roasting process. II. Copper roasting. Equilibria in the system Cu-S-O. W. REINDERS AND F. GOUDRIAAN. *Z. anorg. allgem. Chem.* 126, 85-103(1923).—Phys.-chem. data are given in tables and curves for the system Cu-S-O and found to be similar to those for Pb-S-O. The following equilibria were studied: (1) $2\text{Cu}_2\text{S} + 2\text{SO}_2 \rightleftharpoons 3\text{Cu}_2\text{S} + \text{CuSO}_4$; (2) $\text{Cu}_2\text{S} + 2\text{CuSO}_4 \rightleftharpoons 2\text{Cu}_2\text{O} + 3\text{SO}_2$; (3) $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \rightleftharpoons 6\text{Cu} + \text{SO}_2$; (4) $4\text{CuSO}_4 + \text{Cu}_2\text{O} \rightleftharpoons 3\text{CuOCuSO}_4 + \text{SO}_2$; (5) $\text{CuOCuSO}_4 + \text{Cu}_2\text{O} \rightleftharpoons 4\text{CuO} + \text{SO}_2$; (6) $2\text{CuSO}_4 \rightleftharpoons \text{CuOCuSO}_4 + \text{SO}_3(\text{SO}_2 + \frac{1}{2}\text{O}_2)$, and (7) $\text{CuOCuSO}_4 \rightleftharpoons 2\text{CuO} + \text{SO}_3(\text{SO}_2 + \frac{1}{2}\text{O}_2)$. (2) is normal; with excess SO_2 and pressure (1) is favored; withdrawal of SO_2 from (1) gives (4) and finally (5). CuSO_4 may react according to (4) or decompose according to (6) and (7). The efficiency of the operation depends upon the prevention of (1). Cf. C. A. 9, 1564.

Metallurgy of mercury. ALDO ANTONAZ. *Met. italiana* 15, 266-79(1923).—Theoretical discussion of this subject, with especial reference to the Spirek furnace. This furnace offers the following advantages compared to the reverberatory furnace: (1) The heat is more rationally utilized (saving of fuel). (2) The potentiality of the furnace is greater and its handling simpler (saving of manual labor). (3) Because of the smaller excess of air required and the lesser compression present before the condensers, it gives a smaller amt. of black, and hence a reduction in the loss in the furnace treating the latter (greater yield). Cf. C. A. 17, 2099.

The aluminium age. R. R. FORAN. *Am. J. Pharm.* 95, 285-91(1923).—Historical review. W. A. GAESSLER.

Steel works tar. ED. HERZOG. *Stahl u. Eisen* 43, 1063-73(1923).—Steel works tar now is without exception the so-called prepared tar. The tar is distd. with the recovery of C_6H_6 , phenol, pyridine, naphthalene and anthracene, together with residual oils and pitch. The residual oils (to a large extent creosote oils) are used for wood preservatives and for fuel oil and other mixtures. The types of tars vary greatly in compn. and similarly the pitches vary with the tar, methods of treatment, temp. and methods of distn. The use for the tars here advocated is to cement furnace bottoms and linings for converters. The prepn. of these linings and bottoms has 3 steps: (1) Mixing of tar and dolomite, (2) making the forms or tamping into place, and (3) burning in. In mixing, the tar must be intimately mixed so that only a light coating of tar envelopes the grains of dolomite. It is sometimes necessary to heat the tar of heavy quality in order to get good mixing. In this mixing the fines and coarse material do not sep. out as a rule. In the case of forms, the material may be tamped into place as is the case with some furnaces or in other cases the dolomite tar mixt. may be pressed into the form of bricks or the like, in which case the tar must have a certain binding power. For this reason pitches are used to a great extent as they contain less oils which cause a weakening; on the other hand the pitch should contain enough of the oils so as not to be considered "burned" as it then also has less binding power. Lab. tests are usually resorted to to det. the type of tar. Various methods used for the different tars are discussed and the advantages and disadvantages given. The method of "burning-in" the furnace bottoms is discussed in detail and various methods are given for the remedying of cracking, etc. The method of calcg. the temp. of mixing is described, for use with cold dolomite and hot, as well as the tar. When cold dolomite is used the tar is heated to a higher temp.; with hot dolomite the material is heated in storage bins by having steam pipes throughout the bins. For lab. control the softening temp., the residue on heating, free C content and oil content are detd. A table of analyses of tars from 10 different plants is cited and a discussion is given of their values for this work.

Modern iron and steel works in China. K. E. HUMBERT. *Iron Age* 112, 461-6, 534-7, 598-601(1923). W. A. MUELLER.

Franklin by-product plant. G. A. RICHARDSON. *Coal Age* 24, 309-15(1923).—The Franklin plant of the Cambria Steel Co. is described with illustrations. E. H.

Behavior of manganese in basic open-hearth furnaces. P. OBERHOFFER AND F. KOERBER. *Stahl u. Eisen* 43, 329-34 (1923).—To investigate the conditions of re-absorption by the bath of Mn from the slag, a series of heats was made under carefully controlled conditions and two diagrams are given showing the relation between various Mn reduction factors and the actual reduction. There is no simple relation between the Mn reduction and either the basicity of the slag, the addn. of oxides, the form in which the Mn is added, the ratio between Mn oxide and iron oxide in the slag, or the actual amt. of iron oxide in the slag, as has been variously suggested. No relation was found between the amt. of C in the bath and the O combined with Mn and iron. The problem is obviously complex. It is suggested that the amount of O in the air introduced for combustion has some effect. The Mn content of the bath varies inversely with the iron oxide content of the slag. The duration of the heat increased linearly with the amt. of C present after melting. A linear relation also exists between the total amt. of C oxidized by combustion and the duration of a heat. The amt. of C burned per min. and the rate of rise of temp. of the bath are inversely proportional to the duration of the heat. No relation was found between the rise in temp. of the slag and the duration of the heat. A diagram of tensile tests from various heats shows that the ultimate strength and elongation decrease as the casting temp. rises. J. S. C. I.

Investigation of the manufacture of malleable iron. P. OBERHOFFER AND J. WELTER. *Stahl u. Eisen* 43, 105-10, 301-6 (1923).—The various influences of compn., annealing temps., and oxidizing material used on the properties of the malleable iron, the behavior of S, and the nature of the soft skin formed were investigated. Seven test batches of iron free from graphite were made in a Kryptol furnace and cast in uniform flat bars. One bar was used for chem. analysis and metallographic work and each of the others was converted into malleable iron by a different procedure, then subjected to notched bar tests. The notched bar tests appear to show the following tendencies. Impact figures decrease with increasing S. With similar annealing conditions an active oxidizing medium such as hematite induces a higher impact value than a less active medium, such as mill scale. Increasing the annealing temp., when using a moderately active medium, enables a further increase of the impact value to be attained, which exceeds that obtained by using a more active medium with irons of higher S content. Cupola castings on account of their higher S content should therefore be annealed at higher temps. if ductility is required. Mn practically neutralizes the effect of S. The mechanism of the C changes in relation to the total C, annealing temp., and oxidizing medium are discussed at length. The general effects of S are that with low S, S is absorbed by the iron; with high S as iron sulfide, a decrease in S occurs; while with S as Mn sulfide there is no change. The distribution of S and temper C was investigated by macroscopical and microscopical methods. Detns. of O, S and C in test specimens taken from the interior of the soft skin, together with micro-examin., show the relationships between these elements and also their diffusion. J. S. C. I.

The brittleness of metallic compounds. G. TAMMANN AND K. DAHL. *Z. anorg. allgem. Chem.* 126, 104-12 (1923).—Pressure (A) and impact (B) tests at ordinary temps. and impact and compression (C) tests at elevated temps., supplemented by microscopic examn., were conducted on 25 alloys and single crystals to study the production of parallel or radial lines of deformation with or without intercryst. rupture, the loss of inherent brittleness on heating, and the range of plastic deformation in relation to the m. p. Lines of deformation are generally parallel or radial according to the stress. At ordinary temps., A and B produced many parallel lines in single crystals with Cu_2Zn , and Cu_3Al . B produced both parallel and radial lines with FeSi and Fe_3Si , radial lines only with CuMg , FeSb , FeSb_2 , ZnSb , ZnSb_2 , and parallel lines only with Cu_3Sb , SnSb , and CuAl ; A gave radial lines only with Cu_2Cd and Cu_2Mg . No cases were found where A gave both parallel and radial lines. At 450° B gave radial lines with intercryst. fracture in Cu_3Sn , CuMg , Cu_3Sb and SbSn . C gave the range of plastic deformation in relation to the m. p. for 21 similar alloys; this varied from 50° (NiBi) to 400° (PbS) below the m. p. All compds. lost their inherent brittleness on heating in the vicinity of the m. p.; subsequent cooling resulted in a loss of ductility and resumption of brittleness. Complete data are given in tables and photomicrographs. **Recrystallization in alloys containing a eutectic.** *Ibid* 113-8.—The presence of a eutectic prevents the production of an equally fine-grained structure in alloys as might be produced in a pure metal when recrystn. is effected by annealing after cold working. Cd alloys with Zn, Bi, and Pb were studied; the ratio is approx. 4:3. An increase in the time of annealing from 5 to 120 min. did not effect the elec. resistance of the Cd-Zn (17.4% Zn) eutectic alloy, but gave almost a 100% increase with the Cd-Sn (71% Sn) and the CdPb

(76% Pb) alloys. The production of min. elec. resistance in eutectic alloys does not depend on heating to a definite temp. as with solid soln. alloys. W. A. MUDGE

Recrystallization of metals. G. MASING. *Naturwissenschaften* 11, 413-22 (1923).—The theory of the recrystn. of Sn and Zn after cold-working already advanced by G. (cf. C. A. 16, 3857) is outlined and generalized to apply to the recrystn. of any metal or alloy. C. C. DAVIS

Heat treatment and recrystallization of aluminium. E. WETZEL. *Mitt. Kaiser Wilhelm Inst. Metallforsch.* 1, 24-40(1922).—The relations established between the degree of working, the annealing temp., and the grain size of different metals under definite conditions cannot be generally applied to all metals without modification. The recrystn. diagram is obviously dependent on the grain size of the metal before it has been subjected to stress; material that has been annealed at a lower temp. before being worked than after consists of crystals of uneven size, while that annealed at the same temp. in both the primary and secondary recrystns. consists of grains of uniform size. The rate of heating or of deformation has very little influence on the secondary recrystn. of Al, but the degree of purity has a pronounced effect. Specimens of Al of large grain size have a lower tensile strength than those consisting of small crystals. The formation of very coarse crystals at the surface of cold-rolled Al sheet on annealing has no connection with the degree of rolling. J. S. C. I.

Aluminium containing magnesium. E. HEYN AND E. WETZEL. *Mitt. Kaiser Wilhelm Inst. Metallforsch.* 1, 10-8(1922).—The properties of "Aludur," a specially hardened Al alloy, are compared with those of Al treated by Ger. pat. 244,554 (C. A. 6, 2232); (cf. Brit. pat. 6485, 1910), and it is shown that Al contg. Mg treated by the latter process—quenching from 520°—has all the valuable properties of "Aludur." J. S. C. I.

Structure hypotheses and Röntgen-ray investigations. J. CZOCHRALESKI. *Z. Metallkunde* 15, 60-7, 126-32(1923).—The Laue pattern secured from single crystals of Al that have been strained beyond the elastic limit are much distorted. For crystals subjected to compression, the circular form of the reflection points is changed to that of an ellipse. As the compression increases, these points gradually assume the form of lines radiating from the central spot. Other methods for straining the crystals beyond the elastic limit produce similar distortion in the patterns. F. P. FLAGG

The influence of cold work on the resistivity of metals and alloys. LEON GUILLET AND M. BALLAY. *Compt. rend.* 176, 1800-2; *Rev. métal.* 20, 398-408(1923); cf. C. A. 15, 3065.—The resistivity of pure metals cold hammered as much as possible without producing cracks is slightly greater than that of the metal when annealed. Pb and Sn which are not hardened by cold work show no increase. The increase was not greater than 4%. In general the resistivity of alloys which are solid solns. is increased by cold work. This increase is for most alloys only a few %, yet for the brass 68% Cu, 32% Zn, the increase is 21%. The resistivity of Cu-Ni-Zn alloys is decreased by cold work. This decrease is probably related to a transformation. The resistivity increases as the amt. of cold work increases. F. P. FLAGG

Behavior of iron and copper after repeated tensile stresses at different temperatures. W. MAUSCH. *Mitt. Kaiser Wilhelm Inst. Metallforsch.* 1922, 41-57.—The curve showing the extension of test-pieces of Fe and Cu under repeated loading and unloading is a straight line only during the first application of load. Subsequent applications yield a curve which is concave to the abscissa axis, while the curve of contraction during removal of load is convex to that axis; the curves do not intersect at the axis, there being always a small permanent increase in length after the treatment. The amt. of work that can be done on wrought iron without failure taking place decreases at 200° to half its value at room temp., but rises again to the original value at 300°. In Cu it steadily decreases with rise of temp. J. S. C. I.

Forging and heat treating large sections. W. R. KLINGBACH. *Trans. Am. Soc. Steel Treating* 4, 50-61(1923).—A description of routine operations as practiced in a modern service forge plant provided with up-to-date equipment. Figures and photographs illustrating annealing, forging, and heat treating operations are included. W. A. MUDGE

The mechanism of corrosion. JOHN JOHNSTON. *Ind. Eng. Chem.* 15, 904-5 (1923).—In the study of the corrosion of metals, proper emphasis has not been placed on the influence of effects at the surface of the metal. The study of the equil. in the systems at the surface of a corroding metal and of the elec. resistance and capacity of protective films should yield information that will help in the understanding of the problem. F. P. FLAGG

The hydrogen-ion concentration of natural waters and some etching reagents in

relation to action on metals. W. R. G. ATKINS. *Trans. Faraday Soc.* (advance proof) 1922.—The p_H value for natural waters varies between 6 and 8.3 unless they are more acid as the result of the oxidation of S. Solns. of ferrous salts on standing become more acid, with pptn. of $Fe(OH)_2$. $Fe(OH)_2$ is completely pptd. before $Fe(OH)_3$ as the soln. is made progressively more alk. and the latter is not completely pptd. at p_H 7.1. Thus, a trace of acid suffices to attack iron and the hydroxide produced by hydrolysis is oxidized and pptd. The hydrolysis equil. is upset and the acid is regenerated. An etching soln., prepd. by greatly dilg. a strong acid in order to produce an acid having the desired low p_H value, reacts for only a short time because the p_H value of the soln. is quickly lowered to a point at which the acid will no longer attack the metal. The value of the weak acids as etching agents depends upon the fact that diln. affects the p_H value of a weak acid less than it does a strong one. The action of polishing powders may not be entirely mech. for magnesia gives a soln. close to p_H 10, whereas tonge is apparently nearly neutral.

Corrosion of non-ferrous metals. W. FRAENKEL. *Z. Metallkunde* 15, 161-3 (1923); cf. *C. A.* 17, 2554.—A discussion. F. P. FLAGG

Catalytic action of colloids in corrosion. JOS. K. WOOD. *Chem. Met. Eng.* 29, 188-92 (1923).—A discussion of the colloidal theory of corrosion proposed by Friend (*C. A.* 15, 3013). F. P. FLAGG

The corrosion of iron in the presence of iron sulfide. ROBERT STUMPER. *Compt. rend.* 176, 1316-7 (1923).—Corrosion of Fe in tap and chlorinated mineral waters was accelerated 95 and 68%, resp., at 17° owing to direct contact with FeS . In a 1% NaCl soln. direct contact of FeS with Fe accelerated the corrosion of the latter 230%; indirect contact by means of Fe wire induced strong galvanic action and increased corrosion 470%. The phenomenon is clearly electrochem. W. A. MUDGE

Endurance limit of iron and steel by alternate bending tests compared with the results of tensile tests. R. STRIBBECK. *Z. Ver. deut. Ing.* 67, 631-6 (1923).—A study of fatigue phenomena by the methods used by Moore and Koppers (*C. A.* 16, 1382). F. P. FLAGG

Deterioration of steel and wrought iron tubes in hot gaseous ammonia. J. S. VANICK. *Trans. Am. Soc. Steel Treating* 4, 62-78 (1923).—Prolonged exposure of the metal to hot gaseous NH_3 produced a localized disintegration, the position of which is detd. by the temp. and NH_3 concn. The progress of the deterioration with temp. is similar for both types of material. Details of macroscopic and microscopic features of the deterioration are described in view of their importance in connection with nitrogenized steels. The relations between temp. and the joint reactions representing the decompn. of NH_3 and the nitrogenization of Fe are given to illustrate the general character of the deterioration of steel in heated NH_3 . Photomicrographs are given. W. A. MUDGE

A study of the penetration of steel on quenching. GEORGES CHARPY AND LOUIS GRENET. *Compt. rend.* 174, 1273-6 (1922).—Large bars of Ni and Ni-Cr steels contg. 0.30-0.45% C were water-quenched on one face only; the other sides were slowly cooled by protection with asbestos. Brinell hardness tests show the variation in hardness as a function of the distance from the quenched side. Hardness decreases 40% in the first tenth of the distance from the quenched face and then decreases linearly to a value closely approximating that of the slowly cooled material. W. A. MUDGE

The structural forms of quenched steel. H. HARREMAN. *Stahl u. Eisen* 43, 880-2 (1923).—The data here given are for hardened steel quenched between temps. of 600° and 700°. A steel of 0.64% C, 0.36% Si, and 0.69% Mn, in the form of a square rod 10 cm. long and 1 cm. square cross section, was used for the tests. The etching was done with HNO_3 . The cryst. structures at various quenching temps. were discussed and micrographs are given. Other kinds of steel were tested in the same way. W. A. MUELLER

What have we in the notch percussion test? M. MOSER. *Stahl u. Eisen* 43, 935-42 (1923); cf. *C. A.* 16, 1383.—Two steels, one a Ni-Cr steel and the other a C steel, were taken and the influence of the percussions was noted in each case as curves. These curves show the various characteristics of the two steels. Two steels may be found which differ widely in actual tests but by this method may prove the same. The influence of various heat treatments on these steels and working methods were also investigated, by subjection of various specimens to different heat treatments. The effects were noted by the microscope. W. A. MUELLER

Crystallization of iron and its alloys. I. ALBERT SAUVEUR. *Trans. Am. Soc. Steel Treating* 4, 13-45 (1923).—A description of dendritic crystn. of Fe-C alloys and its further transformation. The properties of steel depend upon its microstructure and

its persistent dendritic segregation; the latter is not effected by the usual heat treatment, while hot working causes deformation of the segregated areas and results in directional properties. The action of certain reagents in dendritic segregations is explained together with the relation existing between the dendritic or solidification structure and microstructure. The article is illustrated with many drawings, photographs, and photomicrographs.

Iron and iron alloys. F. X. MOERK. *Am. J. Pharm.* 95, 515-32, 624-41 (1923).—W. A. MUDG.
Historical review. W. G. GAESSLER

Measurements of small changes in length of quenched duralumin and an aluminium-tin alloy by means of the Martens mirror apparatus. E. HEYN AND E. WETZEL. *Mitt. Kaiser Wilhelm Inst. Metallforsch.* 1, 19-23 (1922).—Quenched duralumin undergoes an appreciable expansion on standing, whereas pure Al shows no noticeable change. An Al-Sn alloy contg. 0.5% Al contracts for some time after quenching, then begins to expand very slowly. J. S. C. I.

Electrochemistry of metallic alloys. III. Anodic behavior of alloys. IV. Cathodic formation of alloys. R. KREMAN. *Metall.* 1922, 107, 115-6, 123-4, 132-3.—From a consideration of the process of anodic soln. of an alloy it is shown that only in rare cases is it possible to sep. the more electropositive from the less electropositive element of an alloy by selective soln., as the soln. potential of a metal operates only on that part of the electrolyte immediately in contact with the surface of the metal. If, however, the less electropositive element becomes detached from the anode and falls to the bottom of the vessel as anode slime then a rough sepn. is possible. The anode slime may contain a considerable amt. of the more electropositive metal owing to its being included in the detached particles of the other metal or to the formation of compds.; at the same time a certain amt. of the least sol. metal will be dissolved. Even when a pure metal is used as anode a certain amt. of anode slime will be formed owing to the casting or working of the metal setting up strains which cause the soln. pressures of different parts of the metal to vary. The laws governing the deposition of alloys on the cathode are discussed and it is shown that only when the cathode consists of a liquid metal, *i. e.*, Hg, can alloys be deposited with certainty at ordinary temps. from aq. solns. In all other cases alloys can be obtained only by depositing the metals in very thin layers and then heating the deposits. J. S. C. I.

Molybdenum as a constituent in alloys. W. GUERTLER. *Z. Metallkunde* 15, 151-4 (1923).—An attempt to det. what metals or alloys could be improved by addn. of Mo yielded negative results. All the metals except those in group 8 of the periodic table are reported on. F. P. FLAGG

Cementation by means of boron. N. PARRAVANO AND C. MAZZETTI. *Atti. accad. Lincei* [v] 31, ii, 424-5 (1922).—When steel is heated at 900° in an atm. of B chloride and H, it becomes coated with a layer of very hard alloy rich in B and capable of cutting glass. Ni also undergoes cementation under these conditions. J. C. S.

Ac₁ range in alloy steels. J. A. JONES. *J. Iron and Steel Inst.* (advance proof) 13 pp. (May, 1923).—In alloy steels Ac₁ occurs over a range of temp. Soaking within this range resolves the carbide into conjugate mixts., 1 of which dissolves. This partial soln. of carbide is associated with partial hardening on quenching and a corresponding change in microstructure. After soaking within the Ac₁ range and cooling below Ar₁ the steel will give 2 Ac₁ points, 1 above and 1 below the normal point. If the steel is quenched from the soaking temp., or is not cooled to Ar₁, only the upper Ac₁ point appears on the heating curve. In certain steels also, provided diffusion has not occurred above Ac₁, a steel normally showing only Ar₁ shows 2 points on cooling. Annealing restores the steel to its original condition. V. O. HOMERBERG

Designing and operating a slag wool plant (LANG) 13. Preparation of ores by flotation (TRAUBER) 13.

BUCHNER, GEORG: *Hilfsbuch für Metalltechniker*. 3rd ed. revised. Berlin: Verlag von Julius Springer. Bound 10s. Reviewed in *Chem. Trade J.* 72, 735 (1923).

The Mineral Industry of the British Empire and Foreign Countries. Statistics, 1919-21. Tin. Imperial Mineral Resources Bureau. London: H. M. Stationery Office. 44 pp. 1s. 6d.

Mineral Industry of the British Empire and Foreign Countries, 1919-1921. Zinc. London: H. M. Stationery Office. 60 pp. 2s.

VAN PATTEN, NATHAN: *The Corrosion of Metals and Its Prevention*. Cambridge: Massachusetts Institute of Technology. 180 pp. \$5.

Apparatus for ore flotation. G. S. A. APPELQUIST and E. V. E. TYDEN. Swed. 53,434, Mar. 21, 1923. A lifting and forcing pump takes the mixt. of liquids and ore from a larger container and applies it into the sepn. vessel in an intermittent current.

Separator for magnetic ores. TEKNISK KEMT A.-B. Swed. 53,433, Mar. 21, 1923. Mech. features.

Extracting metals and alloys. D. W. BERLIN. Brit. 193,057, Feb. 12, 1923. Alloys of Si with Al, Fe, Cr or Mn are used as reducing agents for metallic oxides, particularly oxides or ores of Cr or W, preferably first coned. The powd. materials may be mixed together with suitable fluxes, and may be briquetted with the aid of water-glass or other binder. The reduction may be effected in a bath of molten metal for the production of alloys. Slag is removed from the reduced metal or alloy from time to time, and fresh portions of charge are added.

Treating phosphorous iron ore. F. G. LILJENROTH. Swed. 52,399, Oct. 4, 1922. At first the ore is sepd. magnetically into a slime low in P and a waste high in P. The latter material is reduced in an elec. furnace to a phosphorous pig-iron. The P is partly oxidized to free H_2PO_4 which is used for treating the low-P slime and removing practically all the P from this material. The excess of H_2PO_4 is sepd. by the usual procedure and used for fertilizing or other purposes. Cf. Swed. 51,719.

Treating phosphorous iron ore. F. G. LILJENROTH. Swed. 52,400, Oct. 4, 1922. The low-P slime obtained by the process described above (cf. preceding abstr.) is reduced to pig-iron in an elec. furnace. This pig-iron is mixed with the above mentioned phosphorous pig-iron from the same process or with part of it. The mixt. is worked to steel in a basic converter or by other basic processes. The slag is used as a fertilizer.

Enriching low percentage pyrites in metals and coincidentally recovering sulfur or sulfur compounds. A. RAMÉN and S. G. LILJA. Swed. 52,657, Sept. 6, 1922. The ore is heated in a furnace by roast gases contg. S oxides from another furnace. The heating is regulated so as to transform the ore into a magnetic state. After cooling and grinding the ore is sepd. magnetically. S or its compds. are recovered from the gases. The process can be carried out also in a single furnace.

Zinc, lead and copper from sulfide ores. C. J. CARLSON. Swed. 51,009, Mar. 1, 1922. The ore, which may contain one or more of the named sulfides in combination with Fe sulfides, is treated with hot gases by which Zn and Pb are volatilized. The Cu is then obtained as mat or raw Cu.

Reduction of ore. A. R. LINDBLAD. Swed. 51,351, Apr. 5, 1922. The gas coming out of the furnace or part of it is treated with water at increased pressure. Part of the CO_2 is absorbed by the water and the gas is consequently enriched in CO, and is again forced through the furnace.

Reduction of metal oxides. H. F. ERIKSSON. Swed. 51,431, May 2, 1923. The oxides are heated in an elec. furnace, alone or with solid reducing agents in amts. insufficient for complete reduction. A gas contg. CO is applied in the lower parts of the furnace to complete the reduction.

Reduction of zinc. FINSPONGS METALLVERKS A.-B. Swed. 51,820, May 31, 1922. The materials are preheated in a special elec. heating furnace before they are fed into the reduction furnace.

Condensing arrangement for zinc and lead. E. S. BERGLUND. Swed. 52,749, Sept. 20, 1922. An elec. furnace for the distr. of Zn and Pb is provided with rotating bodies in the lower part of the condenser. These bodies are fitted with blades or shovels and mounted on horizontal shafts driven from outside the furnace. By the violent agitation of the vapors liquid metal is formed.

Condensing apparatus for zinc and lead. E. S. BERGLUND. Swed. 52,750, Sept. 20, 1922. The furnace has a rotary condenser the rotation velocity of which is sufficiently great to sep. the metal particles from the vapors by centrifugal force. The rotary part of the condenser is cup-shaped and is encircled by a channel with an outlet for the liquid metal and an opening for discharging the sepd. oxides.

Removing carbon from chromium. A. R. LINDBLAD. Swed. 52,539, Aug. 23, 1922. Cr or Cr alloys high in C are fused with a metal which forms an insol. or very faintly sol. carbide.

Iron and steel manufacture; furnaces. A. P. HEYEN. Brit. 193,475, Nov. 22, 1921. In mfg. Fe and steel of the type in which Fe ore, silicates or double silicates of Fe are reduced by a suitable gas such as H, CO_2 , etc., the process is carried out in 3 distinct operations separately and one after the other, as follows: (a) a compd. silicate is first obtained by fusing scrap steel, slags from the melting of Pb or Cu, etc., with slags from a former operation; (b) the silicate so obtained is reduced by blowing a suitable reducing gas through the molten mass but above the level of the molten metal;

(c) the metal obtained is refined with substances suitable for the production of the desired product. These operations may be carried out in 3 sep. furnaces but usually are carried out successively in one furnace. A suitable construction is specified.

A strong, dense, acid-proof silicious cast iron. G. SEGERBERG. Swed. 53,896, May 2, 1923. Cu in the form of metal, alloys or compds. is added to a Fe-Si alloy. The resulting alloy should contain at least 6% of Si.

Corrosion preventive for bright steel surfaces. G. SKJOELDBERG. Swed. 53,229, Jan. 3, 1923. Starch or potato flour, graphite and lime are mixed to a fine powder.

Iron alloy. K. A. CASPERSEN. Swed. 51,861, June 7, 1922. The alloy contains 0.22-0.30% C, more than 1.5% Cr, at least 1.0% Si and some Mn, but practically no Ni. Cf. C. A. 16, 552, 1929.

Alloys. W. C. HERAEUS GES. Brit. 193,050, Feb. 10, 1923. Alloys suitable for the points of gold nibs are made by melting together ferro-Si contg. 10-30% of Si with 1-30%, preferably 10 to 15% of 1 or more Pt group metals.

Chromium alloys low in carbon and silicon. AKTIEBOLAGET FERROLEGERINGAR. Swed. 51,642, May 10, 1922. Alloys high in Si are bessemerized. Slags from an advanced state of desilication during one process are applied to the next charge at an earlier point of the process.

Enriching calciferous rocks. B. JOHNSSON. Swed. 53,277, Feb. 28, 1923. The rock is heated to such a temp. that the CaCO_3 is decompd. into CaO, and the cooled materials are sepd. by dry methods.

Welding copper or copper alloys. W. R. J. BRITTEN AND DISTRICT CHEMICAL CO., LTD. Brit. 193,513, Nov. 26, 1921. In welding Cu or Cu alloys, a Cu or Cu alloy filling-rod or wire contg. about 5% of V, or a flux contg. V, is used, or both rod and flux contg. V are used. A suitable flux contg. H_3BO_3 , $\text{Na}_2\text{B}_4\text{O}_7$, NaCl and V is desirable.

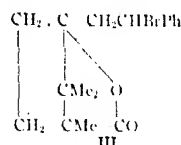
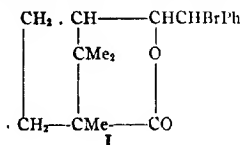
Welding iron. W. R. J. BRITTEN AND DISTRICT CHEMICAL CO., LTD. Brit. 193,512, Nov. 26, 1921. In welding cast Fe with a cast-iron filling-rod or wire, a small quantity of Ti is provided in the rod or wire or the flux, or in both the rod or wire and the flux. A flux contg. Na_2CO_3 and NaHCO_3 , borax, SiO_2 , and Ti is described.

10—ORGANIC CHEMISTRY

CHAS. A. ROUILLER AND CLARENCE J. WEST

The butenic nitriles. P. BRUYLANTS. *Bull. soc. chim. Belg.* 32, 256-60 (1923).—Continuing his former work (C. A. 17, 1427) B. studies the addn. products of NH_3 (or amines) and butenic nitrile (or vinylacetonitrile). The reaction of this nitrile with NH_3 at room temp. is complete only after 3 weeks' standing of the mixt.; at 75° (in a sealed tube) it takes 10 hrs. The reaction product is satd. with K_2CO_3 , dried, and distd. under 18 mm.; the aminobutyric nitrile thus obtained b_{13} 76-77°, d_4^{20} 0.91565, n_D^{20} 1.43533, mol. refraction 23.95 (calcd. 23.97), b. 186° (decompn.). The HCl salt of the base m. 157°; the chloroplatinate m. 236°; the corresponding benzamide, m. 118-9°. This aminobutyric nitrile reduced with Na in alc. gives 1,3-diaminobutane, b. 139-41°, pptg. HgCl_2 as well as picric acid in very dil. soln. The addn. product described above is, therefore, β -aminobutyric nitrile. The same can be proved by sapon. of the nitrile by means of HCl, which yields β -aminobutyric acid. Besides this nitrile, a higher condensation product, b_{13} 177°, is obtained from NH_3 and butenic nitrile; according to its N content (28.03%) and its mol. wt. (158) this product is $\text{NH}(\text{CHMeCH}_2\text{CN})_2$. Ethylamine reacts very violently with butenic nitrile. The ethylaminobutyric nitrile, thus obtained, b_{14} 77-78°, has d_4^{20} 0.8763, n_D^{20} 1.43372, mol. refraction 33.26 (calcd. 33.41), b. 192-3°. In the same way NH_2Me reacts with butenic nitrile; the addn. product b_{14} 82-3°, b. 183-4°. Also NHMe_2 reacts similarly, yielding β -dimethylaminobutyric nitrile b_{13} 79-80°, b. 186-8°, d_4^{20} 0.88180, n_D^{20} 1.4363, mol. refraction 33.23 (calcd. 33.76). The same compd. is obtained from NHMe_2 and MeCH:CHCN . B. preps. the diamino compds. of all these nitriles by reduction with Na and alc., and further the chloroplatinates and HCl salts. By letting MeMgBr act upon β -dimethylaminobutyric nitrile, B. obtains a trimer of crotonic nitrile. Isobutylamine, ethylenediamine and other higher homologs of the substituted amines do not form addn. products with butenic nitrile. However, they act as catalysts in transforming butenic nitrile into crotonic nitrile: $\text{CNCH}_2\text{CH:CH}_2 \rightarrow \text{CNCH:CHMe}$. NMe_3 and piperidine, however, do form addn. products; the former yields the same compd. as NHMe_2 , the latter gives $\text{CNCH}_2\text{CMeNC}_2\text{H}_5$, d_4^{20} 0.9444, n_D^{20} 1.4727, mol. refraction 45.13 (calcd. 44.9), mol. wt. (in acetone) 158. Aromatic amines have no action at all. R. BRUTNER

Brominated lactones from benzylidenecampholic acid. H. RUPE AND A. SULGER. *Helvetica Chim. Acta* 6, 435-42(1923).— γ -(α -Bromobenzyl)- γ -hydroxycampholic acid lactone (I) (*C. A.* 17, 1959), m. 141°, is stable towards KMnO_4 in Na_2CO_3 soln. and is sol. only in warm NaOH or Na_2CO_3 . Reduction with Na-Hg in EtOH contg. H_2O (clear soln.) yields benzylidenecampholic acid (II). MgO and I in a large vol. H_2O for 0.5 hr. give the *Mg* salt of the acid, but if the mixt. is heated for 16 hrs. the δ -lactone of γ -hydroxy- γ -(α -hydroxybenzyl)campholic acid, m. 156°, results. If II is allowed to stand in a desiccator with Br , the di- Br product first results; on longer standing HBr is split off, giving the γ -lactone of the α -bromobenzyl acid (III), m. 206°, which differs considerably in soly. from I; while KOH is without action on I, the Br in III is replaced by HO .



The action of MgO gives a *product* m. 135°, which is Br -free. Reduction by Na-Hg gives II. 3-Hydroxy- γ -(α -hydroxybenzyl)campholic acid, by the action of KOH on III, m. 188°.

Catalytic reduction and hydrogenation. V. G. ANDERSON. *Chem. Eng. Mining Rev.* 15, 365-4(1923).—Catalytic hydrogenation and reduction processes are divided into: Simple hydrogenation (fixation of H in compds. where multiple bonds exist), simultaneous hydrogenation and reduction, and hydrogenation accompanied by the decompn. of the original mol. Examples of each class are given. Catalysts are classified as those which exhibit marked catalytic activity at ordinary temps., those which are markedly active only at elevated temps., and those which, while not exhibiting such marked activity as those of classes 1 and 2, yet stand out from the other elements and are particularly useful as "activators" or "promoters" of catalytic activity. The 3rd class includes Ti , V , Cr , Mn , Mo , W , Th , U , Ce and some rare earth metals. The conditions under which the above elements exhibit greatest catalytic activity are considered.

Acetone—its properties, technology and uses. R. F. REMLER. *Chem. Age* (N. Y.) 31, 342-6(1923).

Reactions of sodammonium with hydrocarbons. P. LEBEAU AND M. PICON. *Compt. rend.* 175, 223-5(1922).—The satd. aliphatic and the CH_2CH_2 hydrocarbons are not attacked by NaNH_2 . The $\text{CH}:\text{CH}$ hydrocarbons form simultaneously a Na deriv. and a satd. hydrocarbon through reduction by the H liberated in the reaction. The aromatic hydrocarbons are not attacked in the ring, but an CH_2CH_2 grouping in the side chain is hydrogenated and a $:\text{CH}$ group reacts as in an open-chain compd. Terpinolene, terpinene, carvene, terebene, α -pinene and menthene do not react. The polycyclic hydrocarbons are variously attacked with ring fissure, hydrogenation, and sometimes formation of Na derivs.

Action of selenium oxychloride upon ethylene, propylene, butylene and amylene. C. E. FRICK. *J. Am. Chem. Soc.* 45, 1795-800(1923).— SeOCl_2 always reacts with olefins according to the equation $2\text{C}_n\text{H}_{2n} + 2\text{SeOCl}_2 = (\text{ClC}_n\text{H}_{2n})_2\text{SeCl}_2 + \text{SeO}$, regardless of whether the SeOCl_2 or the olefin is in excess. The same product is obtained with Se_2Cl_2 , which supports the unsym. structure for the latter: $2\text{C}_n\text{H}_{2n} + 2\text{Cl}_2\text{Se} = (\text{ClC}_n\text{H}_{2n})_2\text{SeCl}_2 + 3\text{Se}$. (ClCH_2CH_2) $_2\text{SeCl}_2$ from C_2H_4 , m. 121.5°; ($\text{ClCH}_2\text{CH}_2\text{CH}_2$) $_2\text{SeCl}_2$ from $\text{MeCH}:\text{CH}_2$, m. 80°. The corresponding compds. from butylene and amylene are so unstable that they could not be isolated.

Action of selenium oxychloride on pure rubber. C. E. FRICK. *J. Am. Chem. Soc.* 45, 1800-4(1923); cf. Lenher, *C. A.* 15, 995.—The reactions between SeOCl_2 and 4 natural rubbers (pale crepe, smoked sheet, para and caucho ball) and a synthetic "isoprene rubber" have been studied. As a result of the treatment with SeOCl_2 the phys. properties of the rubbers change; the products are amorphous powders without elasticity and swelling power and insol. in the ordinary rubber solvents. The pure rubber hydrocarbons from the natural rubbers show slight differences in their reactions with SeOCl_2 , depending upon the source of the rubber and its method of coagulation. Judging by their behavior towards SeOCl_2 there is no difference in empirical compn. between the pure rubber hydrocarbons from natural rubbers and the synthetic product.

C. A. R.

The manufacture of alcohol or ether from ethylene obtained from coal gas. E. DE LOISY AND A. DAMIENS. *Chimie et industrie Special No.*, 664-70 (May 1923); cf. *C. A.* 14, 1115.—Lab. tests showed the most efficient and practical catalysts are 4% of Cu⁺ compds. (especially Cu₂O and Cu₂Cl₂) on the wt. of 66° H₂SO₄ used. C₂H₄ can then be absorbed satisfactorily by scrubbing the gas with acid. The reaction is based on the formation of a complex Cu₂SO₄.nC₂H₄ or Cu₂Cl₂.nC₂H₄. In practice the acid is satd. when it has absorbed 50% of the C₂H₄ corresponding to the equation C₂H₄ + H₂SO₄ = SO₃HC₂H₅. Absorption can be effected at not over 35°, thus preventing formation of isothionic acid, which does not decomp. to EtOH, and preventing decompn. of H₂SO₄. A semi-com. plant was built in a gas works consisting essentially in two scrubbing towers to eliminate H₂O, H₂S and C₂H₂ and C₂H₄ hydrocarbons by means of H₂SO₄, a heater for the gas, and two absorption towers (similar to but higher than the first two) in which was circulated 70° H₂SO₄ with 4% Cu₂O. Results of a 96 hrs. test are described. A diagram is given of a com. installation suitable for the treatment of gas from the carbonization of 400 tons of coal a day. The H₂SO₄ after treatment need not be concd., as it is not too dil. and can be used directly for the manuf. of (NH₄)₂SO₄. Cost is estd. at 70-75 francs a hectoliter of 100% EtOH and 92-118 francs per ton of 100% Et₂O.

α,β-Dichloroethyl ether. V. GRIGNARD AND A. C. PURDY. *Compt. rend.* 175, 200-3 (1922); *Bull. soc. chim.* 31, 982-7.—The previously unknown *α,β*-dichloroethyl ether (I) has been prepd. in 65% yield by satg. a mixt. of 1 mol. ClC₂H₄OH and 1/3 mol. (AcH), with HCl gas at 0-10°. The product sepd. from the aq. layer and dried with CaCl₂ b₁₁ 55-8°. It is a colorless liquid, turning slightly and of penetrating acid odor, hydrolyzes easily in warm water back to its constituents. A small quantity of *β,β*-dichloroethyl acetal (II) is obtained in the above prepu. It is obtained in 38% yield by satg. a mixt. of 0.5 mol. ClC₂H₄OH and 0.25 mol. AcH with HCl according to Fischer and Giebe (cf. *Ber.* 1897, 3053). It b. 196-8° (decompn.), b₁₇ 106-8°, losing HCl readily. With PCl₃ it gives I. I on standing with ClC₂H₄OH gives after 24 hrs. II in 27% yield. The study of homologous compds. and of the possibility of prep. derivs. of *β*-furazolidine is being continued.

Methyl- and ethylammonium-mercuric bromides. R. M. HANN. *J. Am. Chem. Soc.* 45, 1763-4 (1923); cf. Jamieson and Wherry, *C. A.* 14, 1323.—This work was undertaken to complete the series of alkylammonium-mercuric halides and to det. the feasibility of using the bromides instead of the iodides for the sepn. and identification of alkylamines; unfortunately, their extreme soly. in the common solvents precludes their use for such a purpose. Unlike the iodides, the alkylammonium bromides tend to combine with 2 instead of 1 mol. Hg halide. The following alkylammonium-mercuric bromides are described: *Di-Me* (1:2), Me₂NH₂Br.2HgBr₂ from 35 g. HgBr₂ in abs. alc. suspension treated with 9 g. MeBr and MeNH₂.HBr (= 3 g. MeNH₂), m. 171-2°; *di-Et* (1:2), m. 158°; *tri-Me* (1:1), m. 102°, reddens on standing; *tri-Et* (1:2), m. 124-5°; *tetra-Et* (1:1), m. 72°.

A new metallo-organic compound: diplumbic hexaethyl. THOMAS MIDGLEY, JR., C. A. HOCHWALT AND G. CALINGAERT. *J. Am. Chem. Soc.* 45, 1821-3 (1923).—Et₃PbOH in 95% alc. electrolyzed with Pb electrodes and a c. d. of 0.01 amp./cm.² gives diplumbic hexaethyl as a yellowish oil, b₂ about 100°, does not freeze -80°, d. 1.94, is slowly volatile with steam (about 1 cc. with 25-30 cc. H₂O), decomp. easily in air with formation of a yellow powder which rapidly darkens, mol. wt. from 582 for 0.6285 g. in 9.1 g. freezing C₂H₆ to 292 for 0.0182 g. in 14.44 g. C₂H₆ (calcd. 588), gives with HCl Et₃PbCl, PbCl₂ and a gas (C₂H₆).

The urea dearrangement. II. T. L. DAVIS AND K. C. BLANCHARD. *J. Am. Chem. Soc.* 45, 1816-20 (1923); cf. *C. A.* 17, 268.—The reactions which take place between amine HCl salts and urea at 160° have now been found to occur in boiling H₂O also. If urea and PhNH₂.HCl are refluxed in H₂O, PhNHCONH₂ (I) is formed and remains in soln.; after boiling for some time CO(NHPh)₂ (II) begins to sep. This can be filtered off and I obtained by cooling the filtrate. By suitable modifications of the process, repeating the boiling and filtration, it is possible to obtain either or both of the products in excellent yield. Likewise, I refluxed in H₂O gives II just as when it is heated at 160° in dry state. When its aq. soln. is distd. PhNH₂ passes over. A no. of dialkyl-ureas have been prepd. from the alkylamine HCl salts and urea at 160° or in boiling H₂O; the amt. of NH₄Cl produced in the former cases indicated that the reaction had proceeded nearly to completion but the aliphatic ureas are troublesome to manipulate and the yields of actual product were not as good as in the aromatic series. Urea refluxed with NHMe₂.HCl and NHEt₃.HCl gave the corresponding unsym. disubstituted ureas, but in poor yields. There was no evidence of the formation of tetrasubstituted

ureas, however, which is in harmony with the view that unsym. disubstituted ureas dearrange in only 1 way: $RR'NCONH_2 \rightleftharpoons RR'NH + HNCO$. Striking evidence of the dearrangement of substituted ureas is found in the behavior with $PhNH_2$ of $CO(NH_2)_2$ (III). This dearranges in only 1 way: $III \rightleftharpoons EtNCO + EtNH_2$. When it is heated with $PhNH_2$, $EtNH_2$ escapes and the $EtNCO$ combines with $PhNH_2$ to form $EtNHCONHPh$ (IV), which dearranges in 2 ways: $EtNH_2 + PhNCO \rightleftharpoons IV \rightleftharpoons PhNH_2 + EtNCO$. When heated alone the more volatile substances escape and the $PhNH_2$ and $PhNCO$ combine to form II, which is formed more quickly if III or IV is heated with an excess of $PhNH_2$. If 190 g. urea and 390 g. $PhNH_2 \cdot HCl$ in 1 l. H_2O are refluxed until the mixt. bumps, filtered hot from the II, allowed to cool, filtered from the I which seps., again refluxed until bumping occurs, etc., the whole process being repeated 4 times, there are obtained 80.3 g. II, m. 235°, and 218.5 g. I, m. 147°; if, instead of cooling the hot filtrate from each lot of II, it is immediately refluxed again until it bumps, 90% II can be obtained. $CO(NHMe)_2$, m. 99.5–100°, is obtained in 78.4% yield from $MeNH_2 \cdot HCl$ and urea heated 1 hr. at 160–70°; III, m. 112°, in 43% yield from $EtNH_2 \cdot HCl$; $CO(NHBU)_2$, m. 70.5–1.0°, in 79% yield from $BuNH_2$ or its HCl salt refluxed in H_2O with urea; $CO(NHAm)_2$, m. 92.8°, in 0.8 g. yield from the HCl salt of 3.3 g. $AmNH_2$; (iso- $AmNH_2$) $_2CO$, m. 37.5°; $CO(NHCH_2Ph)_2$, m. 167°, in 69.2% yield from urea and 2 equivs. $PhCH_2NH_2$ at 160–70°; $PhCH_2NHCONH_2$, m. 146.6°, in 95.8% yield from $PhCH_2NH_2$ and urea refluxed in H_2O (unlike I it does not change into $CO(NHCH_2Ph)_2$ when boiled in H_2O). C. A. R.

Preparation of alkylguanidines. ROSS PHILLIPS AND H. T. CLARKE. *J. Am. Chem. Soc.* **45**, 1755–7 (1923).—Arndt's new reagent, Me isothiourea sulfate (I) (C. A. **16**, 1073), reacts with NH_2Me and $NHMe_2$ like the alkyl iodide addn. products of thiourea, forming MeSH and methyl- and α,α -dimethylguanidine sulfates (II and III), resp. II, m. 229–40°, is obtained in 500 g. yield from 700 g. I in H_2O suspension with 525 g. of 33% aq. NH_2Me ; the concd. mother liquors and washings with HNO_3 yield a further 90 g. of methylguanidine nitrate, m. 149–50°. III (200 g. from 250 g. I and 285 g. of 33% $NHMe_2$), m. 285–8° (decompn.). MeSH passed into 25% NaOH deposits the salt $2MeSNa \cdot 9H_2O$, long flat needles rapidly efflorescing in the air, decompn. above 200° with formation of considerable Na_2S . C. A. R.

Peralkylated guanidine. I. HANS LECHER AND FRITZ GRAF. *Ber.* **56B**, 1326 (1923).—By using $HgCl_2$ in the Schenck synthesis of pentamethylguanidine (I) (C. A. **16**, 3718) to remove the MeSH from the field of action as fast as formed $[2Me_2NC(=NMe)SMe]_2$ (II) + $2NHMe_2 + HgCl_2 \rightarrow 2Me_2NC(=NMe)NMe_2 \cdot HCl + Hg(SMe)_2$, it is possible to isolate the free I without difficulty. $Me_2NCSNHMe$, m. 87°, is obtained from $NHMe_2$ and $MeNCS$ in purer form by using H_2O instead of alc. as the solvent. Refluxed in H_2O with 1 mol. Me_2SO_4 it gives 85% II, b. 68°. $HgCl_2$ (9 g.), the dry $NHMe_2$ from 25 g. of the HCl salt and 4.4 g. II heated 5 hrs. at 100° in a sealed tube give 35% I, b. 155–60°, very hygroscopic liquid with an amine-like odor, fumes slightly in the air, is easily sol. in H_2O and the usual org. solvents, eagerly absorbs CO_2 from the air, is a strong monoacid base; picrate, yellow, m. 165–6° (cor., decompn.); with MeI in Et_2O it forms hexamethylguanidinium iodide, does not m. 300°, decompn. only at a considerably higher temp., forms an entirely neutral aq. soln., gives no ppt. with H_2SO_4 , $HClO_4$, $(CO_2H)_2$ or picric acid. Attempts to prep. I or its analogs in other ways failed. II with Et_2NMgBr in boiling Et_2O remained mostly unchanged; in boiling PhMe it yielded an evil smelling, basic, S-contg. oil, b. 52°, forming a difficultly sol. picrate, which was probably *N,S'*-dimethyl-*N,N*-diethylisothiourea; treatment of Et_2NMgBr with CO_2 led only to the carbamate stage, Et_2NCO_2MgBr ; Et_2NMgBr in Et_2O with CCl_4 remained mostly unchanged. C. A. R.

Lead tetraacetate as an oxidizing agent. OTTO DIMROTH AND ROBERT SCHWELZER. *Ber.* **56B**, 1375–85 (1923).—While using $Pb(OAc)_4$ in AcOH for oxidimetric titrations (C. A. **16**, 3661), it was noted that the $Pb(OAc)_4$ in Ac_2O is rapidly reduced on boiling with evolution of CO_2 and an inflammable gas. It has now been found that the reaction proceeds mainly according to the equation $Pb(OAc)_4 + Ac_2O \rightarrow Pb(OAc)_2 + (AcOCH_2CO_2)_2O$ (I), i. e., that there is a direct oxidation of a Me to a CH_2OH group. Further study showed that $Pb(OAc)_4$ is especially useful where it is desired to oxidize to HO a labile H atom attached to C. Thus $CH_3(CO_2Et)_2$ is easily oxidized to $AcOCH_2(CO_2Et)_2$ and $AcCH_2CO_2Et$ to $AcCH(OAc)CO_2Et$ (II). HO groups may also be introduced directly into ketones (Me_2CO , $MeCOPh$) but in these cases the reaction is much slower than with $AcCH_2CO_2Et$ and a higher temp. must be used, so that the protection afforded by the acetylation of the HO group is no longer quite sufficient and when equimol. amts. of $Pb(OAc)_4$ and of the substance to be oxidized are used, a part of the latter remains unattacked and another part undergoes further oxidation. Homo-

logs of C_6H_4 (PhMe, CH_2Ph , $CHPh$) can likewise be oxidized to alcs., with very marked differences in the velocity and hence in the homogeneity of the reaction. $Pb(OAc)_4$ will also permit of detecting and measuring with considerable exactness gradations in the lability of a H atom attached to C, for the course of the oxidation can easily be followed volumetrically in homogeneous soln. (AcOH). It is hoped that the power of addn. of double bonds can also be studied in this way; these are oxidized with greatly differing velocity, depending on the substituents present. The $Pb(OAc)_4$ is obtained in 300–50 g. yield from 1.5 kg. well stirred AcOH at 55–65° treated with 600–50 g. Pb_2O_4 in 5–10 g. portions, cooled, filtered, redissolved in 200 cc. AcOH at 50° and allowed to cryst. A considerable further amt. can be obtained, mixed with $PbCl_2$, by treating the mother liquors with Cl; this, crystd. once from AcOH, can be used directly for the oxidations after its $Pb(OAc)_4$ content has been detd. iodometrically. Unlike Ac_2O , AcOH is not appreciably oxidized by the $Pb(OAc)_4$; 5 g. of the $Pb(OAc)_4$ in 50 g. AcOH is reduced only 2.6% after 1.75 hrs. boiling. *O*-Acetylglycolic anhydride (I), b_p 178–80°, is obtained in 5 g. yield from 50 g. $Pb(OAc)_4$ boiled 15–30 min. with 6 parts Ac_2O ; 5% of C_2H_4 (and CO_2) are formed according to the equation $Pb(OAc)_4 \rightarrow Pb(OAc)_2 + 2CO_2 + C_2H_4$. From 44 g. $Pb(OAc)_4$ in 60 cc. AcOH with 8.7 g. Me_2CO is obtained 3.5 g. $MeCOCH_2OAc$ (semicarbazone, m. 146°), while 125 g. $Pb(OAc)_4$, 250 cc. AcOH and 7 g. Me_2CO kept 7 hrs. at 70–80° give about 10 g. $MeCOCH_2OAc$ and 3.6 g. *diacetoxyacetone*, m. 46–7°; semicarbazone, m. 93°. $PhCOCH_2OAc$ is obtained in moderate yield at 80–90° from $PhCOMe$. *Et* α -acetoxyacetoacetate (II), b_p 118–25°, is best obtained in C_6H_6 below 35° (yield, about 24 g. from 30 g. $AcCH_2CO_2Et$ and 92 g. of 96% $Pb(OAc)_4$); it is insol. in H_2O but the H_2O layer, at first neutral, becomes acid after shaking some time, owing to the AcOH split off; it reduces Fehling soln. and NH_2AgNO_3 in the cold; $Cu(OAc)_2$ ppts. no Cu salt but is slowly reduced in the cold with deposition of Cu_2O (this reduction probably proceeds parallel with the splitting off of the Ac group); $FeCl_3$ immediately gives a dirty red-brown ppt.; with Na in Et_2O , H is vigorously evolved on the H_2O bath; with 5% H_2SO_4 , the II decomps. chiefly into $MeCOCH_2OH$, AcOH, $EtOH$ and CO_2 . Semicarbazone of II, solvated crystals from C_6H_6 , can be rapidly crystd. from H_2O and then m. 124° but decomps. on boiling with H_2O . With 1 mol. $PhNHNH_2$ (without a solvent) 3.8 g. II evolves much heat and thickens to a yellow oil, droplets of H_2O sepr.; if 3 more mols. $PhNHNH_2$ are now added and the mixt. is heated on the H_2O bath, NH_3 is evolved and the mixt. becomes brown-red and solidifies after 45 min. to a cryst. magma sepd. by means of C_6H_6 into 1.1 g. of the sol. $PhNHNHAc$ and 1.9 g. of insol. *1-phenyl-3-methyl-4-hydroxy-5-pyrazolone*, m. 225° (decompn.) (the substance obtained by reducing the 4-keto compd. is described in *Ger. pat.* 75,378, as m. 189–93°), sol. in acids without color, in NaOH with yellow color, reduces cold Fehling soln.; heated with 2 mols. $PhNHNH_2$ in 50% AcOH it gives benzeneazo-1-phenyl-3-methyl-5-pyrazolone. *Et* α -acetoxybenzoylacetate, obtained in 45% yield from $BzCH_2CO_2Et$, b_p 140–3°, light yellow, converted by boiling 10% H_2SO_4 into $BzCH_2OH$ and by 3 mols. $PhNHNH_2$ in boiling AcOH into benzeneazo-1,3-diphenyl-5-pyrazolone, red, m. 170–1°. If the reagents and app. are dried with especial care, $Pb(OAc)_4$ dissolves in boiling C_6H_6 with only faint yellow color and on cooling seps. in pure white crystals; 1 g. in 15 cc. C_6H_6 and 1 cc. AcOH is reduced only 1% after 5.5 hrs. boiling. Boiled 4 hrs. with 40 g. PhMe and 200 cc. AcOH, however, 120 g. of 93% $Pb(OAc)_4$ is completely reduced and gives 7.5 g. $PhCH_2OAc$, b. 210–8°. From 40.5 g. of 98% $Pb(OAc)_4$ boiled 1 hr. with 15 g. CH_2Ph and 40 cc. AcOH are obtained 7.5 g. unchanged CH_2Ph and 6.6 g. Ph_2CHOAc , m. 40°. With $CHPh$ the reaction is complete in 20 min. Anethole reacts easily and smoothly below 40° and hydrolysis of the product yields the stereoisomeric *p*- $MeOC_6H_4CH(OH)CH(OH)Me$ (Balbiano, *Atti. accad. Lincei* 16, I, 477–84). Safrole reacts much more slowly than anethole at room temp. (at the b. p. a sudden violent reaction occurs) and stilbene even more slowly. C. A. R.

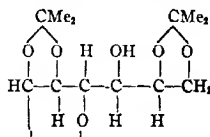
5,5-Diarylbarbituric acids. A. W. DOX AND A. THOMAS. *J. Am. Chem. Soc.* 45, 1811–6 (1923).—*Di-Et diphenylmalonate* (I) and (*p*- MeC_6H_4) $_2C(CO_2Et)_2$ (II) were prepd. by Guyot and Esteve's method (*C. A.* 3, 1279) but all attempts to condense them with urea failed; they seem to lack the stability of the dialkylmalonic esters and when treated with NaOEt and urea lose a CO_2H group. Apparently they are more stable, however, when a HO group is present on the C_6H_4 nucleus and from *di-Et di-p-hydroxyphenylmalonate* (III) was obtained 5,5-di-*p*-hydroxyphenylbarbituric acid (IV). I, obtained in 17.5 g. yield from 30 g. $CO(CO_2Et)_2$ in C_6H_6 and H_2SO_4 heated 7 hrs. at 70°, thick yellow oil, b_p 180–200°, m. 58–9°, with urea and NaOEt in alc. at 106–8° it gave a substance, m. 145°, which was undoubtedly Ph_2CHCO_2H , and Ph_2CONH_2 , m. 169–70°. II, m. 91–2°, likewise yielded (MeC_6H_4) $_2CHCO_2H$, m. 144°, and *di-p*-tolylacetamide, m. 190°. III, from PhOH in $CO(CO_2Et)_2$ satd. in a freezing mixt. with dry HCl, m. 133–4°,

readily sol. in dil. aq. alkali, gives a blue color with FeCl_3 . IV, m. 288–90° (yield, 3.0 g. from 7.5 g. III). *Di-Et diphenoxymalonate* (45 g. from 75 g. $\text{CBr}_2(\text{CO}_2\text{Et})_2$ with 40 g. PhOH and Na in alc.), b₁ 195–204°; 11.5 g. yields 6.5 g. *5,5-Diphenoxymalonate* (V), m. 192°, is intensely bitter. *Di-Et di-4-hydroxy-3-methylphenylmalonate* (16 g. from 14 g. *o*-cresol and 12 g. $\text{CO}(\text{CO}_2\text{Et})_2$ satd. with HCl at 0°), m. 107–8°, gives a blue color with FeCl_3 ; 5 g. yields 1 g. of *5,5-di-4-hydroxy-3-methylphenylbarbituric acid*, m. 217–9°, gives a blue color with FeCl_3 in dil. alc. soln. Neither IV nor V shows noticeable hypnotic properties. C. A. R.

Some dialkylbarbituric acids with tertiary amino grouping. A. W. DOX AND LESTER YODER. *J. Am. Chem. Soc.* 45, 1757–62 (1923).—The object of this work was to add to the dialkylbarbituric acid grouping another grouping of known physiol. activity but united through a stable linkage so that the substances would not readily undergo hydrolysis and enable the 2 components to exert their separate activities independently. *Di-Et ethyl-γ-bromopropylmalonate* (I) (50 g. from 95 g. $\text{EtCH}(\text{CO}_2\text{Et})_2$ and 12 g. Na in C_2H_5 with 200 g. $\text{CH}_3(\text{CH}_2\text{Br})_2$), b₁ 160–74°; 50 g. refluxed 2 hrs. with 30 g. NH_4Et yields 40 g. of the *γ-NEt* deriv., yellow oil, b₁ 143–9°, 10 g. of which, heated 7 hrs. at 108° in an autoclave with 3 g. urea and 2.5 g. Na in alc., gives 3.5 g. *5-ethyl-5-γ-diethylaminopropylbarbituric acid*, m. 165–6°. *Di-Et ethyl-γ-acetanilino-propylmalonate*, from Na and PhNHAc in C_2H_5 refluxed 12 hrs. with I, viscous yellow oil, b₁ 244–50°; 12 g. with urea and Na in alc. gives 9 g. *5-ethyl-5-γ-acetanilino-propylbarbituric acid*, m. 180°. *Di-Et ethyl-γ-acetophenetidinopropylmalonate*, b₁ 237–40°; 13 g. yields 8.8 g. *5-ethyl-5-γ-acetophenetidinopropylbarbituric acid*, m. 158–9°. *Di-Et isoamyl-γ-bromopropylmalonate* (II) (50 g. from 75 g. iso- $\text{AmCH}(\text{CO}_2\text{Et})_2$), b₁ 175–82°; 30 g. gives 29 g. of the *γ-NEt* deriv., thick yellow oil, b₁ 155–61°, 11 g. of which yields 5 g. *5-isoamyl-5-γ-diethylaminopropylbarbituric acid*, m. 133°. *Di-Et isoamyl-γ-ethylaminopropylmalonate* (15 g. from 25 g. II and 18 g. PhNH_2 heated 4 hrs. at 160°), yellow, b₁ 194–201°; 10 g. yields 3 g. *5-isoamyl-5-γ-ethylaminopropylbarbituric acid*, m. 135°. *Di-Et isoamyl-γ-acetophenetidinopropylmalonate* (18 g. from 24 g. II), viscous yellow oil, b₁ 245–60°; 10 g. yields 5 g. *5-isoamyl-5-γ-acetophenetidinopropylbarbituric acid*, m. 155°, unchanged by successive treatment with hot alkali and concd. HCl . The above barbituric acids have a bitter taste similar to that of veronal but have no hypnotic effect, probably as a result in some cases of insol. and hence lack of absorption, in others of a reversal of the distribution coeff. C. A. R.

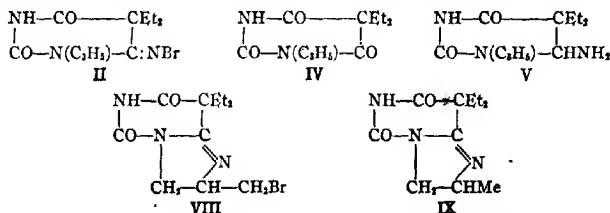
The sulfuric esters of sugars. VI. Acetone compounds of glucose sulfates. HEINZ OHLE. *Biochem. Z.* 136, 428–48 (1923); cf. C. A. 17, 71.—To 1 g. diacetone-glucose in 75 cc. pyridine is added 4 cc. ClSO_3H in 20 cc. EtOH -free CHCl_3 at a temp. under 0°. After standing overnight at room temp. the solvents are evapd.; the pyridine salt of diacetoneglucose 3-sulfate (I), m. 163–4° (decompn.), $[\alpha]_D^{20}$ –21.9° (CHCl_3), also prepd. by shaking 3.3 g. II (below) with 3 g. CuSO_4 in 150 cc. Me_2CO 36 hrs. A double salt with NaOAc , $\text{C}_6\text{H}_7\text{O}_6(\text{C}_2\text{H}_5\text{SO}_3)_2\text{Na} \cdot \text{NaOAc}$, produced in small amts. when a slight excess of NaOAc is added to I in EtOH , m. 221–2° (decompn.), $[\alpha]_D^{20}$ –13.37° (H_2O). Na salt, prepd. from I with Na_2CO_3 , m. 208° (decompn.), $[\alpha]_D^{20}$ –14.69° (H_2O); brucine salt, prepd. from I in CHCl_3 , m. 248° (decompn.), $[\alpha]_D^{20}$ –27.63° (H_2O), $[\alpha]_D^{20}$ –30.98° (CHCl_3). When I in alc. is heated 1 min. and cooled slowly, the pyridine salt of mono-acetoneglucose-3-sulfate (II) seps. in needles, m. 134°, $[\alpha]_D^{20}$ approx. –13.50° (H_2O). Ba salt (III), extd. with MeOH and pptd. with excess EtOH , contains 5 mols. EtOH , $[\alpha]_D^{20}$ –13.99°; at room temp. 1 mol. EtOH is lost, when $[\alpha]_D^{20}$ –14.39°. Na salt of monoacetoneglucose 6-sulfate is prepd. like I, from 4.5 g. monoacetoneglucose and 1.35 cc. ClSO_3H . The sirup (IV) obtained on evapn. of solvents is dissolved in EtOH , and heated with 5 g. NaOAc in 10 cc. H_2O . The residue on evapn. is taken up in EtOH as a fine suspension, which is cleared with 100 cc. Me_2CO . After standing on ice, any NaOAc is removed and, after concn., CHCl_3 added to incipient pptn. The crystals which sep. are recrystd. from EtOH with the addn. of a few drops of H_2O . They contain 0.5 mol. H_2O , m. 157° (decompn.), $[\alpha]_D^{20}$ –9.88°. Ba salt is prepd. by shaking IV in cold H_2O with PbO and BaCO_3 . To the filtrate is added hot satd. Ag_2SO_4 , then H_2S in the presence of BaCO_3 . Pyridine is removed from the filtrate by Et_2O . After concn. the crystals are reprecipd. from EtOH by Et_2O at low temp. They contain 1 mol. EtOH , $[\alpha]_D^{20}$ –7.23°. When to 2 g. of the Ba salt in 20 cc. H_2O is added 15 cc. satd. $\text{Ba}(\text{OH})_2$ and 2.3 g. strychnine sulfate, and the filtrate from the alk. soln. evapd., the strychnine salt, from hot EtOH , m. 182° (decompn.), $[\alpha]_D^{20}$ –25.19° (H_2O), seps. The strychnine salt of glucose 6-sulfate is prepd. when 8.7 g. III stands overnight with a

soln. of 9.6 g. strychnine acid sulfate. After neutralization with $\text{Ba}(\text{OH})_2$ and evapn., needles contg. 1 mol. H_2O sep. on standing at low temp., $[\alpha]_D^{25} -6.27^\circ$, falling to $[\alpha]_D^{15} 0.72^\circ$. Ethyl hydrogen sulfate brucine salt is pptd. contg. 0.75 mol. H_2O after 1.5 g. II is boiled 4 hrs. in 25 cc. EtOH. It m. $201-5^\circ$ (decompn.), $[\alpha]_D^{20} -29.80^\circ$ (H_2O). The brucine salt, prepd. after deacetonization of III by standing with 0.1 N H_2SO_4 , is identical with that of Soda (C. A. 17, 2872). It is suggested that the acid takes an active part in the acetonization of β -glucose by breaking up the furan ring. This leaves C_1 free for the Me_2CO ; at the same time an ester is formed on C_4 . When now the 1,2,5,6-diacetone compd. is formed, the lactone ring cannot be formed on C_1 since Ac is attached to it. The following formula is suggested as a possibility. Until further proof for this is forthcoming Karrer's formula best fits the facts.



GEORGE ERIC SIMPSON

Course of the bromination of allyl-substituted iminobarbituric acids. OTTO DIELS. *Ann.* 432, 115-36 (1923).—The condensation of $\text{H}_2\text{NCONHC}_2\text{H}_5$ and $\text{NHC-EtCO}_2\text{Et}$ in the presence of EtONa , by heating 3 hrs. in a pressure flask at $102-5^\circ$, gives *C,C*-diethyl-3-allyl-4-iminobarbituric acid (I), m. 109° . Two atoms Br in AcOH gives the *N*-bromide (II), m. 184° (1st isolated as the *HBr* salt, decomp. about 250°), and some dibromide (III) $\text{N}:\text{CCEtCONHCHNHCH}_2\text{CHBrCH}_2\text{Br}$, m. 120° , which does not form a *HBr* salt. The constitution of II follows from the facts that dil. acids do not split off NH_3 , that treatment with Zn dust in EtOH gives *N*-allylveronal (IV), m. $79-80^\circ$, and that careful reduction with Al-Hg in EtOH gives the amine (V), m. 131° (contains approx. 0.5 mol. H_2O of crystn.), and the carbinol $\text{C}_{11}\text{H}_{19}\text{O}_3\text{N}_3 \cdot 0.5\text{H}_2\text{O}$ (VI), m. 174° (oxalate, contg. $2\text{H}_2\text{O}$). Phenylisocyanate of V, $\text{C}_{11}\text{H}_{19}\text{O}_3\text{N}_3 \cdot \text{PhNCO} \cdot \text{H}_2\text{O}$, m. 220° . HNO_3 and V give VI, which is oxidized by CrO_3 in AcOH at 60° to IV. If the oxidation is carried out at 80° a compd., m. 185° , is obtained. Boiling 50% AcOH converts V into NH_3 and VI. If the crude condensation product, from which I is obtained, is poured into AcOH, there is obtained a small amt. of the compd. $\text{C}_{11}\text{H}_{17}\text{O}_3\text{N}_3 \cdot \text{AcOH} \cdot 2\text{H}_2\text{O}$ (VII), decomp. 245° . Careful addn. of NH_3 to the aq. soln. and crystn. from EtOH gives I. This indicates that in the condensation there is formed a mixt. of 2 isomers. Bromination of VII gives the bromide (VIII), m. $151-2^\circ$, the *HBr* salt of which decomp. about 265° . Reduction of the Br compd. with Zn and EtOH gives the base (IX), m. 246° . When I is warmed with *HBr* in AcOH (satd. at 0°), there results a base, $\text{C}_{11}\text{H}_{17}\text{O}_3\text{N}_3$, m. 165° (*HBr* salt, m. 285°). *C,C*-Diethyl-3-allyl-4,6-diiminobarbituric acid (X), m. 257° , results from $\text{H}_2\text{NCONH}_2\text{H}_2$ and $\text{Et}_2\text{C}(\text{CN})_2$. Allowed to stand 2-3 days in 20% H_2SO_4 , IV is formed. *HBr* in AcOH and X give the *HBr* salt, $\text{C}_{11}\text{H}_{19}\text{ON}_4 \cdot \text{HBr}$, decomp. above 255° ; H_2SO_4 likewise converts this into IV. Br



added to an aq. suspension of X gives a bromide *HBr* salt, which is reconverted into X by concd. NH_4OH . The condensation of dibromopropylurea and $\text{NCCCH}_2\text{CO}_2\text{Et}$ or $\text{Et}_2\text{C}(\text{CN})_2$ gives the compd. $\text{C}_8\text{H}_7\text{ON}_3\text{Br}$, m. 146° . C. J. WEST

Methylethylketone-xyloses and mixed ketonylated compounds of xylose. OLOF STANBERG AND KNUT SJÖBERG. *Ber.* 56B, 1448-53 (1923); cf. C. A. 17, 2703.—From

10 g. xylose shaken with 300 cc. MeCOEt and 10 cc. concd. H_2SO_4 are obtained 3-4 g. 1,2-methylethylketone-xylose (I), insol. in petr. ether but sol. in AcOEt, and about 4 g. 1,2,4,5(?)-di[methylethylketone]-xylose (II), sol. in petr. ether. I $b_{D, 20}$ 127-9°, does not reduce Fehling soln. directly, $[\alpha] -8.0^\circ$ in H_2O for the Hg yellow line. II $b_{D, 20}$ 104-6°, $[\alpha] 17.4^\circ$; the velocity of its partial hydrolysis by HCl is of the same order of magnitude as that of diacetone-xylose; shaken with an amt. of dil. HCl insufficient for its soln. it is gradually hydrolyzed quant. to I. 1,2-Acetone-4,5(?)-methylethylketone-xylose (2.5 g. from 5 g. acetone-xylose treated 8 hrs. with 150 cc. MeCOEt and 5 cc. H_2SO_4), $b_{D, 20}$ 104-5°, sol. in about 125 parts H_2O , $[\alpha] 16.1^\circ$. 1,2-Methylethylketone-1,5-(?)-acetone-xylose, from I in Me_2CO and H_2SO_4 after 2 hrs., $b_{D, 20}$ 102-4°, sol. in 80 parts H_2O , $[\alpha] 15.7^\circ$. The Messenger iodometric method for detg. Me_2CO can be applied equally well to the above MeCOEt derivs. after hydrolysis with H_2SO_4 (a small correction must be made for the I used up by the carbohydrate—about 5% of the total I consumed in the case of the mono- and 3.5% in that of the diketone compds.).

C. A. R.

The pentosans. III. Purity of xylan from straw. E. HEUSER AND M. BRADEN. *J. prakt. Chem.* 104, 259-64 (1922); cf. *C. A.* 16, 1082.—The presence of methylxylan is detd. as methylfurfural phloroglucide (Tollens and Ellet, *J. Landw.* 53, 130 (1905)) which is sol. in alc. The presence of lignin is detd. by the action of HI on its MeO groups. The prepn. of xylan by Salkowski's method, using Fehling soln., being very costly, H. tried the method of pptg. with HCl from alc. NaOH, which Schulze (*Z. physiol. Chem.* 16, 403 (1892)) claimed to give a product of < 0.6% ash. H. found, however, much higher ash in this product, up to 6.0%.

O. B. HELFELICH

Polysaccharides. XVIII. Lichenin. P. KARKER AND H. JOOS. *Biochem. Z.* 136, 537-41 (1923); cf. *C. A.* 17, 988.—Lichenin prepd. from *Cetraria islandica* is very closely related to ordinary cellulose. The chief difference is that it dissolves in hot H_2O to form a colloid soln.

GEORGE ERIC SIMPSON

The sugar contained in tuberculinic acid, the nucleic acid of tubercle bacilli. F. B. BROWN AND T. B. JOHNSON. *J. Am. Chem. Soc.* 45, 1823-7 (1923); cf. *C. A.* 17, 1261.—The tuberculinic acid was subjected to all the purification processes commonly used for the purification of other nucleic acids until it showed a const. P and N content (8.11 and 11.3%, resp.). In the products of its acid hydrolysis were identified levulinic acid and HCO_2H , showing that the sugar in it is a hexose. Quant. detn. of the pyrimidines confirmed the previous results (9.7% cytosine, 11.8% thymine and no uracil).

C. A. R.

Behavior of cyclopropanecarboxylic acid at the anode and the thermal decomposition of perbutyric acid. FR. FICHTER AND HANS REEB. *Helvetica Chim. Acta* 6, 450-7 (1923).—It has been established that electrolysis of the K salt of cyclopropanecarboxylic acid produces at the Pt anode a type of Kolbe synthesis, whereby in the presence of excess of cyclopropanecarboxylic acid the allyl ester of this acid is formed. The more probable product, the cyclopropyl ester, is not formed because of the instability of cyclopropanol, which is converted into isomeric allyl alc. The allyl ester is accompanied by considerable quantities of higher boiling products, which are probably polymers, and from which no single recognizable substance has thus far been sepd. The formation of esters by electrolysis of salts of the fatty acids is due to the presence of the primary peracids which are decompd. with the formation of alcs., but which in the presence of excess acid form esters.

C. R. PARK

The rule of the conservation of substitution type of the benzene nucleus. A. F. HOLLEMAN. *Rept. Brit. Assoc. Advancement Sci.* 1922, 359-60.—The rule can be applied without restriction only to the introduction of a 2nd substituent in PhX. Pure *p-o*-substitutions and *m*-substitutions are regarded as limits. All substitutions actually observed are more or less mixed. The substitution-type remains unchanged as long as there is formed more than 60% *p-o*-compds. for the *p-o*-type and 40% *m*-compd. for the *m*-type. Exceptions appear to be the introduction of Et in PhCl by the Friedel-Crafts reaction and the mercuration reactions of Dimroth, but such exceptions are only apparent. When there are 2 substituents, X and Y, already present, the validity of the rule can be judged only if the ratios in which the isomerides are formed by the introduction of a 2nd group into PhX and PhY are known. The rule is difficult of application where more than 2 substituents are present.

C. C. DAVIS

Reactions of strongly electropositive metals with organic substances in liquid ammonia solution. III. Reduction of nitrobenzene by sodium in liquid ammonia. G. F. WHITE AND K. H. KNIGHT. *J. Am. Chem. Soc.* 45, 1780-7 (1923); cf. *C. A.* 17, 2108.—Pure $PhNO_2$ dissolves in liquid NH_3 without color and on slow treatment with 4 atoms Na the soln. becomes bright red: $PhNO_2 + 4Na + NH_3 = PhNNaONa(I)$

+ NaNH_2 + NaOH . If the reaction mixt. is treated with H_2O PhN:NPh and $\text{Ph}_2\text{N}_2\text{O}$ are obtained as the result of secondary reactions of PhNHOH (1.8 g. $\text{Ph}_2\text{N}_2\text{O}$ from 3.6 g. PhNO_2 and 2 g. Na ; 0.9 g. Ph_2N_2 from 3.6 g. PhNO_2 and 2.8 g. Na). With NH_4Cl in NH_3 instead of H_2O , however, the product is PhNHOH (36%): $\text{PhNNaONa} + 2\text{NH}_4\text{Cl} = \text{PhNHOH} + 2\text{NaCl} + 2\text{NH}_3$. With an excess of MeI the NH_3 soln. of **I** yields an unstable oil having certain of the characteristics of the primary product of the action of MeI on $\text{PhN}(\text{O})\text{Me}$ (Bamberger and Tschirner, *Ber.* 32, 1882(1899)), which may be formed according to the scheme $\text{I} \rightarrow \text{PhNMeOMe} \rightarrow \text{PhNMe}(\text{OMe})\text{I}$. **K** with PhNO_2 or KNH_2 with PhNHOH in NH_3 likewise give a red cryst. ppt., probably PhNKOK . With 6 atoms of Na , PhNO_2 gives PhNNa_3 , yielding PhNH_2 with H_2O . That NaNH_2 is formed in the reduction of PhNO_2 was shown by the isolation of a small amt. of $1\text{-C}_{10}\text{H}_7\text{NH}_2$ when $\text{C}_{10}\text{H}_7\text{Br}$ was added to the reaction mixt. The soln. of **I** in NH_3 yields PhNO_2 with air. PhNO readily gives **I** with 2 atoms Na in NH_3 . PhNHOH is reduced to PhNH_2 by 2 atoms of Na ; $\text{Ph}_2\text{N}_2\text{O}$ gives 77% Ph_2N_2 ; Ph_2N_2 yields 75% $(\text{PhNH})_2$ with 2 atoms Na and with 4 atoms forms PhNNa_3 (identified by conversion into PhNEt_3 with EtI); $(\text{PhNH})_2$ with 2 atoms Na forms PhNH_2 , addn. of EtI to the reaction mixt. giving a mixt. of PhNH_2 and PhNHEt , which indicates the formation of PhNHNa . C. A. R.

β -Nitroarylhydroxylamines. I. β -2,4- and β -2,6-Dinitrophenylhydroxylamine. W. BORSCH. *Ber.* 56B, 1494-501(1923); cf. preceding abstr.—While β -m-nitroarylhydroxylamines are easily obtained under certain conditions by partial reduction of *m*-dinitrobenzenes it has never been possible to prep. the *o*- and *p*-comps. in this way, but it has now been found that they can easily be obtained from the extraordinarily reactive 2,4-dinitrophenol ethers. Thus, 2,4-(O_2N) $_2\text{C}_6\text{H}_3\text{OMe}$ or [2,4-(O_2N) $_2\text{C}_6\text{H}_3\text{O}$ warmed with alc. NH_2OH quant. gives β -2,4-dinitrophenylhydroxylamine (**I**), orange-red, decomp. 80°, stable for weeks in solid form but extraordinarily sensitive in soln., especially on warming, evolving N oxides and forming dark red to brown-black resins; NH_2OH and N_2H_4 salts, $\text{H}_2\text{NCONHNH}_2\text{HCl}$, etc., prevent this decompn., probably by rendering harmless the small amts. of N oxides which are formed when the decompn. begins and which then catalytically accelerate it. **I** dissolves in concd. H_2SO_4 without color change but ice ppts. orange flocks drying on clay to amorphous red-brown clumps different from the original **I**. It dissolves in alkalis, alkali carbonates, acetates, etc., with deep red-brown color, forming stable salts and repptd. by mineral acids. *Na salt*, from **I** in Et_2O with Na in abs. alc., black powder, sol. in H_2O with dark green color, deflagrates on heating. The aq. soln. gives with many other cations deeply colored ppts., one of the most characteristic of which is the blue-black *Ba salt*. *NH₄ salt*, $\text{C}_6\text{H}_3(\text{O}_2\text{N})_2\text{NH}_4\text{C}_2\text{H}_5\text{O}_2\text{N}$, black needles with green surface luster, m. 142° (foaming); *PhNH₂ salt*, $\text{C}_6\text{H}_3(\text{O}_2\text{N})_2\text{PhNH}_2$, dark red, m. 111-2° (decompn.). **I** (0.5 g.) in boiling NH_4OH with $(\text{NH}_4)_2\text{S}$ gives 0.3 g. 1,2,4- $\text{C}_6\text{H}_3(\text{NH}_2)_2\text{NO}_2$, m. 199-200°. CrO_3 in AcOH oxidizes **I** to 1-nitroso-2,4-dinitrobenzene, dark yellow, m. 133° to a deep green liquid solidifying on cooling to a yellow cryst. drop, sol. in warm alc., Me_2CO , C_6H_6 with pure green color paling to yellow or brown-yellow on cooling, sol. in alkalis with deep red-brown color with decompn. Slowly added to fuming HNO_3 (d. 1.54) and heated on the H_2O bath 3 hrs., 5 g. **I** gives 4.5 g. 1,2,4- $\text{C}_6\text{H}_3(\text{NO}_2)_3$, light yellow, m. 60°. With 8 parts Ac_2O at room temp., **I** quant. yields the *O*-acetate, yellow, reddens on heating and m. 164° (gas evolution), sol. in cold alkalis and carbonates, in NH_4OH on gentle warming, with blood-red color, quickly changing to dark brown as the *Ac* group is split off, is (unlike **I** itself) only slowly attacked by hot Ac_2O , yielding, together with much dark brown resin, the *di-Ac deriv.* of **I**, yellowish white, m. 141°, insol. in alkalis. *O-Benzoyl* (from 2 g. **I** and 1.4 g. BzCl in $\text{C}_6\text{H}_6\text{N}$), dark yellow, m. 163-4° (slow gas evolution); 2 mols. BzCl give a reddish resin. *Methyl ether* of **I** (2.5-2.6 g. from 4 g. **I** with alk. Me_2SO), dark yellow, m. 110-1°, sol. in hot NH_4OH with dark brown color, seps. unchanged on cooling, gives 1,2,4- $\text{C}_6\text{H}_3(\text{NH}_2)_2\text{NO}_2$ with $(\text{NH}_4)_2\text{S}$, yields in Et_2O with CH_3N_3 the *O,N-di-Me deriv.* of **I**, light yellow, m. 87°, insol. in dil. NaOH . *β -Bz deriv.* of the *Me ether*, light yellow, m. 155°. **β -2,6-Dinitrophenylhydroxylamine (II)** (3.1 g. from 5 g. 2,6-(O_2N) $_2\text{C}_6\text{H}_3\text{OPh}$), orange-red, decomp. 115°, somewhat more stable in org. solvents but less in the solid form than **I**, sol. in hot H_2SO_4 with light yellow color, cautious diln. with ice H_2O pptg. bright red needles which decomp. 95°; *di-Bz deriv.*, yellowish, m. 108-9°. With fuming HNO_3 , 0.8 g. **II** gives 0.7 g. 1,2,3-trinitrobenzene, yellowish, m. 121°, converted by PhNH_2 in MeOH on the H_2O bath into 2,6-(O_2N) $_2\text{C}_6\text{H}_3\text{NHNHPh}$, m. 106-7°. C. A. R.

Constitution of the dichlorohydroxyethylidenebisnitroanilines. A. S. WHEELER AND S. G. SMITH. *J. Am. Chem. Soc.* 45, 1839-42(1923); cf. C. A. 14, 181.—It had been shown that when the isomeric *o*- and *p*- NO_2 Schiff bases obtained by the condensa-

tion of CCl_3CHO and the nitroanilines are treated with alc. KOH, NaOMe or NaOEt, 1 of the Cl atoms is replaced by OH, OMe or OEt. No compds. are known that contain Cl and OH attached to the same C atom and it seemed probable that in the compds. in question the HO has migrated to the α -C atom and that they have the structure $\text{CHCl}_2\text{C}(\text{OH})(\text{NHC}_6\text{H}_4\text{NO}_2)_2$. This has been confirmed by heating them 2 min. with 30% H_2SO_4 . In this way the *dichlorohydroxyethylidenbis-p-nitroaniline* (I), m. 178°, gives *p*- $\text{O}_2\text{NC}_6\text{H}_4\text{NH}_2$ and 80% *p*-nitrodichloroacetamide, $\text{O}_2\text{NC}_6\text{H}_4\text{NHCOCCHCl}_2$ (II), pale yellow, m. 127°, unstable towards alkalis but stable towards acids, also obtained in the same way from the Me and Et ethers of I and from $\text{CHCl}_2\text{CO}_2\text{H}$ and *p*- $\text{O}_2\text{NC}_6\text{H}_4\text{NH}_2$ refluxed 10 min. with P_2O_5 . Similarly, the *o*- NO_2 isomer, m. 143°, of I and its Me or Et ethers give with H_2SO_4 70% of the *o*- NO_2 isomer of II, bright yellow, m. 70–72°, also obtained in 6 g. yield from 5 g. *o*- $\text{O}_2\text{NC}_6\text{H}_4\text{NH}_2$ and 5 g. $\text{CHCl}_2\text{CO}_2\text{H}$ with P_2O_5 . *m*- NO_2 isomer of II, from *m*- $\text{O}_2\text{NC}_6\text{H}_4\text{NH}_2$, $\text{CHCl}_2\text{CO}_2\text{H}$ and P_2O_5 , m. 103°. C. A. R.

Isosterism of phenyl isocyanate and diazobenzene-imide. W. H. CAROTHERS. *J. Am. Chem. Soc.* **45**, 1734–8 (1923).—If Ph isocyanate (I) has the structure $\text{Ph}:\text{N}::\text{C}::\text{O}$ and diazobenzene-imide (II) the structure $\text{Ph}:\text{N}::\text{N}::\text{N}$ instead of $\text{Ph}:\text{N}::\text{N}::\text{N}$, or, in terms

of Lewis' theory of at. structure, the 2 compds. are to be represented by the formulas $\text{Ph}:\ddot{\text{N}}::\text{C}::\ddot{\text{O}}::$ and $\text{Ph}:\ddot{\text{N}}::\text{N}::\ddot{\text{N}}::$, then the 2 mols. have the same no. of extra nuclear electrons arranged in the same way and differ only in the magnitude of the nuclear charges of the atoms, and they should therefore be very similar in their phys. properties. As a matter of fact, their abs. densities (d.), vapor pressures (*p*) and viscosities (η) plotted against the temps. give smooth curves which are in each case almost exactly parallel. The results calcd. from the formulas below agree with those found practically within the limits of exptl. error ($\pm 0.03\%$ for d. and $\pm 0.7\%$ for *p* and η): d.: I, $-0.001044t + 1.1152$; II, $-0.1044t' + 1.1152$ ($t' = t - 2.44^\circ$). *p*: I, $157 - 4.76t + 0.042t^2$; II, $157 - 4.76t' + 0.042t'^2$ ($t' = t - 1.7^\circ$). η : I, $1.326 - 0.02163t + 0.000174t^2$; II, $1.326 - 0.02163t' + 0.000174t'^2$ ($t' = t - 4.8^\circ$). These results confirm the view that the substances are isosteric and also that II has the open-chain structure, although this should probably be written $\text{Ph}:\text{N}::\text{N}::\text{N}$, as predicted by Langmuir (*C. A.* **14**, 1481), instead of $\text{Ph}:\text{N}::\text{N}::\text{N}$. C. A. R.

Alkyl and aliphatic migration in the reduction of nitrobenzoyl phenylhydrazones. GEORG LOCKEMANN. *Z. angew. Chem.* **36**, 349–51 (1923).—Reduction expts. with Zn and H_2SO_4 on *p*-nitrobenzoyl ethylenephénylhydrazine, designed to establish the α -position of the $\text{COC}_6\text{H}_4\text{NO}_2$ group and expected scission of the mol. at the union of the 2 N atoms with formation of $\text{PhNHCOC}_6\text{H}_4\text{NH}_2$ and NH_2Et , resulted in the formation of *p*- $\text{PhNHCOC}_6\text{H}_4\text{NH}_2$, according to the equation: $\text{PhN}(\text{COC}_6\text{H}_4\text{NO}_2)_2\text{N}:\text{CHMe} + 10\text{H} = \text{PhNHCOC}_6\text{H}_4\text{NH}_2 + \text{NH}_3 + 2\text{H}_2\text{O}$, thus showing migration of the Et to the N of the NO_2 group. In explanation of this reaction 2 suggestions are offered, i. e., *intramolecularly*, the Et group migrates from the hydrazine N which splits off to form free NH_3 to the N of the same mol. which is reduced from NO_2 to NH_2 , or *intermolecularly*, in that nascent A^+H is hydrolytically sepd. from the hydrazine complex, thereupon uniting with the nascent NH_3 to an ethyleneamino compd., a so-called Schiff base, which finally takes on H_2O to yield the EtNH compd. For reasons for the foregoing interpretations (cf. Miller and Ploechl, *Ber.* **25**, 2020; Schultz, *Ber.* **16**, 2600; v. Miller, *Ber.* **25**, 2072). Similar behavior on reduction was observed in the case of α -*p*-nitrobenzoyl- β -ethylidene-*p*-tolylhydrazine (cf. Kuegler, *Diss. Berlin* 1923) and the *p*- $\text{O}_2\text{NC}_6\text{H}_4\text{CO}$ deriv. of propylidenephenylhydrazine, involving in each case migration of alkyl to reduced N of the NO_2 group. Further examples of purely aromatic hydrazones are given in the behavior of the 3 isomeric *p*-, *m*- and *o*- $\text{O}_2\text{NC}_6\text{H}_4\text{CO}$ derivs. of benzylidenehydrazine on reduction. With Zn dust and dil. H_2SO_4 , the reaction in the case of the $\text{O}_2\text{NC}_6\text{H}_4\text{CO}$ compd. was mainly, that of the *m*- and *o*-compds. entirely in accordance with the equation: $\text{PhN}(\text{COC}_6\text{H}_4\text{NO}_2)_2\text{N}:\text{CHPh} + 10\text{H} = \text{PhNH}(\text{COC}_6\text{H}_4\text{NH}_2) + \text{NH}_3 + 2\text{H}_2\text{O}$, while with AcOH instead of H_2SO_4 , the reaction followed in large measure (*p*. 60%, *m*. 35%, *o*. 42%) the equation: $\text{PhN}(\text{COC}_6\text{H}_4\text{NO}_2)_2\text{N}:\text{CHPh} + 10\text{H} = \text{PhNHCOC}_6\text{H}_4\text{NH}_2 + \text{NH}_3 + 2\text{H}_2\text{O}$. W. O. E.

Properties of arspenamine. W. G. CHRISTIANSEN. *J. Am. Chem. Soc.* **45**, 1807–11 (1923).—Arsphenamine (I) forms with Me ketones (Me_2CO , MeCOEt , MeCOPr , MeCOBu , $\text{MeCOCH}_2\text{CHMe}_2$) additive compds. in which the ketone is held very firmly; it is removed neither by drying at room temp. or 98° nor by reprecip. from an Me_2CO -free solvent with Et_2O . When I and Na_2AsO_3 in H_2O are treated with HCl and H_3PO_4 , the yellow color gradually changes to red and a polyarsenide of I is formed, the rate of the reaction depending upon the method of prep., the I and seeming to depend upon its phys. properties. The amt. of 1:1 HCl required to ppt. I from dil. aq. soln. is const.

when 1 method of prepn. is strictly followed but slight variations in certain steps in the synthesis cause fluctuations in the amt. of acid required. This titration has therefore been found useful in detg. the closeness with which the routine method of prepn. has been followed. The phys. properties of I are affected materially by the amt. of HCl used in converting the base into the HCl salt; it is advantageous to use slightly more than 2 mols.

C. A. R.
Aromatic diarsonic acids and their reduction products. III. H. LIEB AND O. WINTERSTEINER. *Ber.* 56B, 1283-91 (1923); cf. *C. A.* 17, 1446.—*4-Nitrophenylene-1,2-diarsonic acid*, from diazotized $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}_2$ coupled with the aid of Cu powder with Na_2AsO_4 , needles with 1 H_2O ; heated above 100° , it loses 2 H_2O , forming the anhydride. Yield (as the anhydride), 55%. Reduced by Kalb's method (*C. A.* 15, 2635), it gives 55% of the *4-NH_2 acid*, seps. with 1 H_2O , changes above 100° into the anhydride, gradually darkens above 300° , can be diazotized and couples with β -naphthol to a red dye; on the H_2O bath with H_3PO_2 (d. 1.28) it yields *4-amino-1,2-arsenophenylene* or *4,4'-diamino-1,2,1',2'-diarsenobenzene*, yellow amorphous substance sol. in very dil. HCl with formation of the HCl salt and reprecipitated by alkalis, insol. in most org. solvents but easily sol. in cold $\text{C}_6\text{H}_5\text{N}$, decomps. above 280° ; attempts to det. the mol. wt. in boiling $\text{C}_6\text{H}_5\text{N}$ failed, probably owing to the formation of a colloidal soln. *2-Hydroxyphenylene-1,4-diarsonic acid*, obtained in 60% yield from the 2- NH_2 acid diazotized in H_2SO_4 and heated on the H_2O bath, reddens about 220° , does not m. 315° , reduced by H_3PO_2 to *2-hydroxy-1,4-arsenophenylene* or *2,2'-dihydroxy-1,4,1',4'-diarsenobenzene*, red-brown amorphous substance easily sol. in alkalis, EtOH, Me_2CO , AcOH, $\text{C}_6\text{H}_5\text{N}$ and concd. H_2SO_4 , the solns. oxidizing in the air with extraordinary rapidity, becoming colorless and depositing amorphous yellow ppts. *2-Chlorophenylene-1,4-diarsonic acid*, from the 2- NH_2 acid diazotized in HCl and allowed to stand with Ullmann's Cu-bronze, crystals with 0.5 H_2O , gradually becomes reddish about 210° and sinters but does not m. 315° , also obtained, but in very poor yield, from diazotized 3,4-Cl(H_2N) $\text{C}_6\text{H}_3\text{AsO}_4\text{H}_2$ and Na_2AsO_4 . *2-Bromophenylene-1,4-diarsonic acid*, from the diazotized 2- NH_2 acid and KBr, crystals with 0.5 H_2O . The Cl acid with H_2PO_2 gives an amorphous lemon-yellow ppt., insol. in H_2O , dil. or concd. H_2SO_4 and org. solvents, sol. with decolorization in boiling concd. H_2SO_4 or HCl and in AmOH; dried at 105° in *vacuo* it analyzes somewhat high in H and low in C and As for the expected *chloro-p-arsenophenylene* or *dichlorodiarsenobenzene*.
 C. A. R.

Some mercury derivatives of phenol ethers. F. C. WHITMORE AND BURRUS MIDDLETON. *J. Am. Chem. Soc.* 45, 1753-5 (1923); cf. *C. A.* 15, 1713.—Protection of the HO groups in mercurated phenols by alkylation has the same effect as protection by acylation, i. e., the stability of the C-Hg linkage towards iodides, thiocyanates and thiosulfates is increased. Mercurated phenol ethers with these reagents give the corresponding Hg bis-compds. and solns. contg. inorg. Hg but no alkali. The Hg bis-compds. are formed much more readily from the *o*- than from the *p*-compds. *o*-ClHgC₆H₄OH (5 g.) with 3.5 g. EtI and 0.7 g. NaOH in 50% alc. gently heated 1 hr. gives 7 g. *o*-IHgC₆H₄OEt (I) and a little (*o*-EtOC₆H₄)₂Hg (II) and 5 g. of *p*-ClHgC₆H₄OH similarly gives 5 g. of a mixt. of the corresponding *p*-compds. which it is difficult to sep. From 8 g. *o*-ClHgC₆H₄OH, 1 g. NaOH and 3 g. MeI are obtained 7 g. *o*-IHgC₆H₄OMe (III) and 1 g. (*o*-MeOC₆H₄)₂Hg (IV). Refluxed 6 hrs. with KI in alc. 4 g. III yields 1.5 g. IV, m. 108° , and 2 g. I after 1 hr. gives 1.5 g. II, m. 81° . With KSCN 2 g. III in 3 hrs. gives 1.5 g. of a product m. $75-80^\circ$, and 1.6 g. I yields 0.8 g. II. I (2 g.) dissolved in aq. $\text{Na}_2\text{S}_2\text{O}_3$ deposits 1.2 g. II. Heated 15 min. in alc. with HgCl₂, IV gives *o*-ClHgC₆H₄OMe, m. $177-8^\circ$, and II yields *o*-ClHgC₆H₄OEt.
 C. A. R.

Exchange of OR for other radicals in nitrophenol ethers. W. BORSCH. *Ber.* 56B, 1488-93 (1923).—The action of NH_3 , PhNH_2 , N_2H_4 , PhNHNH_2 , and $\text{AcCHN}(\text{CH}_3)\text{CO}_2\text{Et}$ was tried on the following compds. under conditions as nearly the same as possible: 2,4-Dinitroanisole (I), from 2,4-(O_2N)₂ $\text{C}_6\text{H}_3\text{Cl}$ and Na in MeOH, yellowish, m. 88° ; [2,4-(O_2N)₂ $\text{C}_6\text{H}_3\text{O}$] (II), obtained almost quant. from (O_2N)₂ $\text{C}_6\text{H}_3\text{Cl}$ in C_6H_6 boiled 8 hrs. with Na in PhOH; 2,3,5-MeO(O_2N)₂ $\text{C}_6\text{H}_3\text{Me}$ (III), light yellow, m. 72° (10 g. from 10 g. *o*-MeOC₆H₄Me by nitration according to Stadel, *Ann.* 217, 154 (1883)); 4,3,5-MeO(O_2N)₂ $\text{C}_6\text{H}_3\text{Me}$ (IV), light yellow, m. 123° (10 g. from 19.8 g. AgO(O_2N)₂ $\text{C}_6\text{H}_3\text{Me}$ with MeI in MeOH); 4,3-MeO(O_2N)₂ $\text{C}_6\text{H}_3\text{CN}$ (V), yellowish white, m. 152° (17 g. from 13.3 g. MeOC₆H₄CN in cold HNO_3 (d. 1.52)); 4,3-MeO(O_2N)₂ $\text{C}_6\text{H}_3\text{CO}_2\text{Et}$ (VI), m. $99-100^\circ$, from the acid, m. $186-7^\circ$, which is obtained in 19 g. yield from 15.2 g. MeOC₆H₄CO₂H in HNO_3 ; 3-nitro-4-phenoxybenzonitrile (VII), yellowish, m. 79° ; *Et* 3-nitro-4-phenoxybenzoate (VIII), light yellow, m. $93-4^\circ$. I (1 g.) heated 1 day in a loosely stoppered flask with 15 cc. alc. and 2 cc. concd. NH_4OH at $40-50^\circ$ gave just enough (O_2N)₂ $\text{C}_6\text{H}_3\text{NH}_2$ for a m. p. detn.; II behaved in the same way. With PhNH_2 , I is

practically unchanged after 2 hrs. at 150° and at 180° forms a dark red resinous mass from which no cryst. substance could be isolated; 1.3 g. II yields 1 g. $((\text{O}_2\text{N})_2\text{C}_6\text{H}_3)_2\text{NH}$; III and IV are recovered in part, V almost completely, unchanged. With $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, I in hot alc. is almost quant. converted in 0.5 hr. into $(\text{O}_2\text{N})_2\text{C}_6\text{H}_3\text{NHNH}_2$; 2.6 g. II gives 2 g. $(\text{O}_2\text{N})_2\text{C}_6\text{H}_3\text{NHNH}_2$ and PhOH ; 1.06 g. III gives with 0.3 g. $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ a moderate, with 0.6 g. $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ an almost quant. yield of the *N*-*H*₄ salt, yellow needles, of *p*-methyl-6-nitrobenzasimidol, $\text{Me}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{N}:\text{N}:\text{NOH}$, light yellow, decomp. 225°; IV gives

6-methyl-4-nitrobenzasimidol, light yellow, m. 241° (decomp.); 1.78 g. V with 0.6 g. $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ yields 1.5 g. $\text{H}_2\text{NNH}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{CN}$, m. 221–2°, also obtained in 1.78 g. yield from 2.4 g. VII; 2.35 g. VI gives 1.22 g. and 2.87 g. VIII gives 1.8 g. $\text{H}_2\text{NNH}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{CO}_2\text{Et}$, m. 103°; 3 g. *o*- $\text{O}_2\text{NC}_6\text{H}_4\text{OME}$ in alc. at the b. p. gives 0.7 g. and at 140–50° 1.8 g. benzasimidol (IX), m. 110°, also obtained in 1.4 and 2 g. yield, resp., under the same conditions from *o*- $\text{O}_2\text{NC}_6\text{H}_4\text{OPh}$ and in 1.1 and 2 g. yield from *o*- $\text{O}_2\text{NC}_6\text{H}_4\text{Cl}$. IX seps. in hydrated needles, m. air-dry 104° (gas evolution), resolidifies and m. again 157–8°. *p*- $\text{O}_2\text{NC}_6\text{H}_4\text{OME}$ with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in alc. at 105° is $\frac{1}{2}$ converted into IX. I (2 g.) heated 2 days in alc. with PhNHNH_2 gives so little 2-phenyl-5-nitrophenylazimidobenzene (X) that it could not be isolated pure but it can be obtained from II; 1.06 g. III yields 0.15 g. of the 7-Me deriv. of X, brownish yellow, m. 161°; IV, V and VII do not perceptibly react after 2 days' boiling. With $\text{AcCH}(\text{C}_6\text{H}_5)(\text{NO}_2)_2\text{CO}_2\text{Et}$ in alc. 6 g. I in C_6H_6 after 3 days gives $\text{AcCH}(\text{C}_6\text{H}_5)(\text{NO}_2)_2\text{CO}_2\text{Et}$, m. 97–8° (together with 5.8 g. unchanged I), also obtained in 3.25 g. yield (with 0.7 g. II) from 7.8 g. II; III does not appreciably react after 4 weeks.

C. A. R.
Compounds of styphnic acid with hydrocarbons. N. N. EFREMOV. *J. Russ. Phys. Chem. Soc.* 51, 353–98 (1919).—E. divides the investigated systems into 3 groups: those forming (1) a stable compd., (2) an unstable one, (3) no compds. at all. The data obtained are: Group 1: C_{10}H_8 ; eutectic p. (e. p.) 13.6° and 148.8°; compd. equimol., 165.5°; 2nd e. p. 95.7° and 79.2°. Phenanthrene; 1st e. p. 29.3° and 125.6°; compd. equimol., 132.7°; 2nd e. p. 81.7° and 85.7°. Anthracene; 1st e. p. 15.5° and 151.4°; compd. equimol., 176.3°; 2nd e. p. 54.6° and 170.1°. Acenaphthene; 1st e. p. 21.7° and 136.1°; compd. equimol., 156°; 2nd e. p. 89.3° and 89.5°. Retene; 1st e. p. 33.6° and 125.6°; compd. equimol., 135.7°; 2nd e. p. 83.4° and 76.2°. Group 2: $\alpha\text{-C}_{10}\text{H}_7\text{Cl}$; allotropic change at 20–40° and 92.2°; transition p. (t. p.) 53.6° and 109.8°; no e. p.; $\alpha\text{-C}_{10}\text{H}_7\text{Br}$; allotropic change at 20–50° and 70.9°; t. p. 57.3° and 101.2°; almost no e. p.; $\beta\text{-C}_{10}\text{H}_7\text{Br}$; t. p., 49° and 131.7°; e. p. 97.8° and 56.9°. $\text{C}_{10}\text{H}_7\text{CH}_2\text{Ph}$; a t. p., possibly a clear distectic, (1:1) at 134.3°; e. p. at 98.4° and 47.5°. Fluorene; t. p. 47.5° and 127.5°; e. p. 75.6° and 97.1°. Stilbene; t. p. 45° and 142.4°; e. p. 80.8° and 114.6°. Group 3: $\alpha\text{-C}_{10}\text{H}_7\text{NO}_2$; e. p. 84.3° and 45.2°. α -Nitroacenaphthene; e. p. 47.7° and 80.3°. Ph_2 ; e. p. 83.4° and 61.5°. $(\text{PhCH}_2)_2$; e. p. 93.6° and 50.7°. 1,3,5- $\text{Ph}(\text{NO}_2)_3$; e. p. 64.0° and 83.2°. 2,4,6-Trinitrotoluene; e. p. 87.7° and 67.5°. 2,4,6-Trinitroxylenes; e. p. 38.2° and 141.0°. Ph_2CH ; gap in liquid miscibility 14.5–50.5° and 167.4°; e. p. 96.0° and 94.2°. CH_2Ph ; gap in l. m. 40.2–57.0° and 144.6°; e. p. 97.5° and 22.6°.

M. G. KORSUNSKY
Compounds of picric acid with hydrocarbons. N. N. EFREMOV. *J. Russ. Phys. Chem. Soc.* 50, 1, 372–421 (1918).—The method of study was that of thermal analysis of the binary mixts. involved. The mol. structure of the picrates of hydrocarbons was found to be of the general type of 1:1. The existence of the previously known picrates of $\alpha\text{-C}_{10}\text{H}_7\text{Cl}$, of α - and $\beta\text{-C}_{10}\text{H}_7\text{Br}$ and of $\alpha\text{-C}_{10}\text{H}_7\text{CH}_2\text{Ph}$ was corroborated by this method, and it was shown that the fusion curves of these picrates are characterized by "distectic" points, i. e., temps. at which crystn. begins, corresponding to m. ps., at 125.7, 81.5, 129.6, 83.5, and 97.0°, resp. Phenanthrene, acenaphthene, acenaphthylene and retene yielded picrates whose fusion curves possess sharply defined maxima at 132.8, 160.8, 165.3 and 120.9°, resp. The presence of a NO_2 group in the hydrocarbon nucleus acts unfavorably upon its combination with picric acid, (I) as was shown by the failure to obtain a picrate of nitroacenaphthene and by the instability and decompn. on fusion of the picrate of $\alpha\text{-C}_{10}\text{H}_7\text{NO}_2$. Ph_2 and $(\text{PhCH}_2)_2$ do not give picrates. The picrate of stilbene, $\text{C}_{14}\text{H}_{12}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_3\text{OH}$, was prepd. for the first time, but it is unstable and decomposes on fusion at 92.8°. Ph_2CH and PhCH do not yield picrates, and when in a liquid state they dissolve (I) but to a slight extent (not given). The thermal diagram of the system I- Ph_2CH shows at 112.6° 2 triple points for mixts. contg. 10 and 71.5%, resp., of PhCH . Within these 2 limits of concn. the mixts. sep. into 2 liquid layers. The upper crit. temp. for the system is at 140.3° and contg. 40% of the hydrocarbon; the eutectic point is at 82.3° and 90.6% concn. Compounds of picryl chloride with hydrocarbons. N. N. EFREMOV. *Ibid* 421–40.—Hydrocarbons combine with

$C_6H_5Cl(NO_2)_2$, (II), in the mol. ratio of 1:1. The existence of previously known compds. of II with $C_{10}H_8$ (m. 91.2°), phenanthrene (m. 82.4°), and fluorene (m. 64.6°) is corroborated by thermal analysis of the corresponding binary systems. Chlorylpicrates of anthracene (m. 141.6° (decompn.)), acenaphthene (m. 113.2°), acenaphthylene (m. 109.4°), and of retene (m. 53.5°) were discovered in the fusion mixts. On fusion I and II yield solid solns. in various concns. up to 24.3% of II in I and to 14.3% of I in II. **Compounds of picramide with hydrocarbons.** N. N. EFREMOV. *Ibid* 441-59.—Picramide (III) combines with hydrocarbons, similarly to I and II, in the mol. ratio of 1:1. The existence of compds. of III with $C_{10}H_8$ (m. 168.8°) and with anthracene (m. 158.8°) is corroborated by the thermal method employed. New compds. of III with phenanthrene (m. 160.2°), acenaphthene (m. 195.4°), retene (m. 125.1°) and with fluorene (unstable, m. 127.5° (decompn.)) were prepd. When fused, I and III are inter-sol. The limiting soly. concns. of the solid solns. are by wt. 16% of I in III and 11.5% of III in I. The following table gives a comparative resumé of the various compounds studied or prepd., the m. ps. and their resp. position on the thermal diagram (max. or transition pt.) and the color of the compds. (Y yellow, R red, O orange, B brown, P purple).

1 mol. hydrocarbon	I	1 mol. tri-NO ₂ compd. II	III	Triaitroresorcinol
Naphthalene	Max. 147.-149.5 Y	Max. 91.2 amber-Y	Max. 168.8 bright Y	Max. 165.5 golden Y
Phenanthrene	Max. 132.8 O-R	Max. 82.4 O-R	Max. 160.2 R	Max. 132.7 O
Anthracene	Trans. pt. 152.0 R	Trans. pt. 141.6 brown-R	Max. 158.8 blood-R	Max. 176.3 ruby-R
Acenaphthene	Max. 160.8 O	Max. 113.2 O	Max. 195.4 bright-R	Max. 156.0 O-Y
Acenaphthylene	Max. 165.3 O-Y	Max. 109.4 O	—	—
Fluorene	Max. 84.0 O	Max. 64.6 golden-Y	Trans. pt. 127.5 Y-B	Trans. pt. 127.5 B-R
Retene	Max. 120.9 Y-B	Max. 53.5 Y-B	Max. 125.1 brick-R	Max. 135.7 P-R

The importance of the colors of these compds., previously neglected, is emphasized.

W. A. PERLZWEIG

Diacyl derivatives of *o*-hydroxybenzylamine. L. CHAS. RAIFORD AND E. P. CLARK. *J. Am. Chem. Soc.* 45, 1738-43(1923); cf. *C. A.* 17, 1446, and earlier papers.—In the more than 15 *o*-aminophenols in which it has been found that benzylation (by the Schotten-Baumann method) of the *N*-Ac derivs. results in the Bz radical attaching itself to the N and the Ac group migrating to the O, both reacting groups (NH₂ and OH) were attached directly to the C_6H_4 ring. *o*-HOC₆H₄CH₂NH₂ (I) has now been studied as an example of a phenol with an unsubstituted NH₂ group in an *o*-side chain and it has been found that it does not exhibit the migration of the acyl groups so characteristic of the diacylated *o*-aminophenols. *o*-HOC₆H₄CH₂NOH, m. 57°, is obtained in 98% yield by Loch's method. With 2.5% Na-Hg in alc. below 55° it gives 96% of I, m. 129°. *o*-Acetoxybenzylacetamide (2.8 g. from 2 g. I, 8 g. Ac₂O and 2 drops concd. H₂SO₄), m. 192-3°, hydrolyzed quant. by slightly more than 2 mols. KOH in alc. in 5 min. to HOC₆H₄CH₂NHAc (II), m. 140°. *o*-BzOC₆H₄CH₂NHAc, m. 116° (yield, 93%), gives with 2.25 mols. KOH in alc. after 0.5 hr. 89.5% II. *o*-Hydroxybenzylbenzamide (III), obtained in 43.4% yield from I in Et₂O with 0.5 mol. BzCl in H₂O, m. 142°. *o*-Benzoyloxybenzylbenzamide, from I, 2.1 mols. KOH and 2.15 mols. BzCl in H₂O, m. 142-3°, yields III quant. with 2.25 mols. KOH in alc. in 20 min. III with NaOAc-Ac₂O gives 97% *o*-acetoxybenzylbenzamide, m. 85°, yielding with 2.25 mols. KOH in alc. after 30 min. 91% of III. C. A. R.

Production of imido thiol esters by the condensation of thiocyanates with resorcinol or phloroglucinol. R. J. KAUFMANN WITH ROGER ADAMS. *J. Am. Chem. Soc.* 45, 1744-52(1923).—Alkyl and aryl thiocyanates, RSCN, condense readily with m -C₆H₃(OH)₂ (I) and *sym*-C₆H₃(OH)₂ in the presence of HCl and ZnCl₂ to form imido thiol ester HCl salts of the type (HO)₂C₆H₃C:(NH.HCl)SR. In order to remove the Zn completely from the crude products, they must be reprecipitated from cold HCl. Part of this Zn is present as a salt of the phenol and in 1 case such a salt was actually isolated. The general method of procedure consisted in bubbling dry HCl for 30-40 hrs. through 1 mol. each of phenol and thiocyanate and 0.2-1.0 mol. ZnCl₂ in Et₂O in a flask provided with a stirrer and reflux condenser attached to a H₂SO₄ drying bottle. *Me* thiol-*p*-

resorcylateimide-HCl (130–60 g. crude product from 110 g. I, 73 g. MeSCN, 136 g. ZnCl₂ and 275 cc. Et₂O), m. 244–5° (decompn.) (all m. ps. are cor.); *sulfate*, from the HCl salt in H₂O with H₂SO₄, m. 230–1.5°. *Et ester-HCl* (140–60 g. from 110 g. I), m. 229.5–31.5° (decompn.); *sulfate*, m. 214–7°. *Bu ester-HCl*, m. 266–8° (decompn.). (The *Bu thiocyanate*, obtained in 85–90% yield from BuBr and NH₄SCN, b.₇₆ 184.5–5.5°, d_4^{25} 0.9563, n_D^{25} 1.4636.) *Ph ester-HCl* (12 g. from 22 g. I), m. 220–2° (decompn.); the crude product is apparently the Zn salt, C₁₅H₁₀O₂NCISZn, light yellow crystals from 96% alc.-concd. HCl, m. 225–7° (decompn.). *Me thiol-2,4,6-trihydroxybenzoate-imide-HCl* (36.3 g. from 35 g. II), m. 255–6°. Aq. NaHCO₃ converts the above HCl salts into the free esters: *Me thiol-β-resorcylate-imide*, yellow, m. 197–9° (decompn.); *Et ester*, yellow, m. 196–7° (decompn.); *Bu ester*, bright yellow, m. 173–4° (decompn.); *Ph ester*, yellow, m. 156–8° (decompn.); *Me thiol-2,4,6-trihydroxybenzoate imide*, cream-colored, m. 223–6°. The HCl salts refluxed 2–5 hrs. with very dil. HCl (8–10 hrs. in the case of the deriv. of II) are converted into the thiol esters: *Me thiol-β-resorcylate* (25 g. from 35 g. of the imide-HCl), needles with 1 H₂O, m. 70–1° and, anhyd., 97–8°; *bis-p-nitrobenzoate*, m. 214–6°. *Et ester*, m. 60–1°; *bis-p-nitrobenzoate*, m. 190–1°. *Bu ester*, light brown oil; *bis-p-nitrobenzoate*, m. 115–6°. *Me thiol-2,4,6-trihydroxybenzoate*, m. 190°. The thiol imides refluxed in the corresponding alc. are converted into the *O*-esters: *Me β-resorcylate-imide*, (HO)₂C₆H₃C(=NH)OMe, from (HO)₂C₆H₃C(=NH)SMe or the Bu ester in MeOH, m. 210°; *HCl salt*, apparently hydrated crystals from 15% HCl, m. 166–8° and, after drying *in vacuo*, 224–6°. *Et ester*, m. 214°. Refluxing with dil. HCl converts these imido esters into the CO₂R compds. *Me β-resorcylate*, m. 116–7°; *Et ester*, b.₇₆ 170–6°, m. 69–70°. The above (HO)₂C₆H₃CO₂Me (10 g.) with 10% KOH at 70° gives after 30 hrs. 4 g. 2,4-(HO)₂C₆H₃CO₂II, m. 215–7°. C. A. R.

Catalytic reduction of acid chlorides. K. W. ROSENEMUND and FRITZ ZETZSCH. VI. **Preparation of unsaturated aldehydes.** K. W. ROSENEMUND and G. WEILER. *Ber.* 56B, 1481–7(1923); cf. C. A. 16, 2842.—*O-Acetylanilil chloride*, obtained in 92% yield from the acid refluxed 2 hrs. with 2 parts SOCl₂, m. 57°. *Anilide*, m. 160–1°. *Amide*, m. 175°. The chloride (2 g.) with 0.7 g. Pd-BaSO₄ catalyst in 10 cc. PhMe, 10 mg. "quinoline-S" and H gives in 2.5 hrs. 1.1 g. vanillin, m. 80° (the acetate could in no case be isolated). PhOCH₂COCl, b.₇₆ 142°, similarly hydrogenated 3.5 hrs. at 133° yields PhOCH₂CHO (isolated as the NaHSO₃ compd. in 72% yield). Anisaldehyde is obtained in 81% yield. PhCH=CHCOCl at 122° under 560 mm. gave with quinoline-S 56%, with crystd. thioquinanthrene 60% of the aldehyde (as the NaHSO₃ compd.). *o-Chlorocinnamyl chloride* (yield, 72%), b.₇₆ 155–60°, m. 40°; *anilide*, m. 176°; *aldehyde* (obtained in 92% yield as the NaHSO₃ compd.), m. 50°; *oxime*, m. 96°; *oxime acetate*, m. 71–2°. The aldehyde is also obtained in 25% yield from *o*-ClC₆H₄CHO and AcH allowed to stand in alc. with a few drops of NH₄Et for 3 days. The oxime in EtOH-AcOH slowly treated with 4% Na-Hg gives *γ-o-chlorophenylpropylamine*, isolated as the HCl salt, m. 167°. *Salicyloxyacetyl dichloride*, b.₇₆ 174°, m. 60°; *anilide*, m. 171–2°. Attempts at hydrogenation failed. C. A. R.

Some new derivatives of synthetic adrenaline (suprarenine). CASIMIR FUNK and LOUIS FREEDMAN. *J. Am. Chem. Soc.* 45, 1792–5(1923).—Ethers of the type 3,4-(HO)₂C₆H₃CH(OR)CH₂NHMe have been prepd.; they differ from adrenaline (I) in that they form sol. and easily oxidizable bases and have therefore to be isolated and purified as the HCl salts; it has not as yet been possible to convert them back into I by hydrolysis. *dl-3,4-Dihydrophenylethanolmethylamine-HCl*, obtained in 65% yield from *dl*-I.HCl refluxed 0.5 hr. with 1.5 mols. HCl in abs. alc., m. 169° (cor.), gives the same color reactions as I, is sol. in 2.5 parts abs. alc. When the I.HCl was refluxed 1 hr. with 4 mols. HCl there was obtained, as by-product, 3 g. of *diadrenaline ether-HCl*, O[CH(CH₂NHMe.HCl)C₆H₃(OH)₂]₂, m. 180–3°, gives with FeCl₃ a deep green color changing to reddish violet and then violet on standing or adding NH₄OH, forms with HgCl₂ and NaOAc a grayish blue ppt. darkening on standing, gives with NH₄OH alone a gray ppt. sol. in excess of NH₄OH with purple color, yields a grayish white ppt. with phosphotungstic and phosphomolybdic acids. *Me ether* of I.HCl obtained in 26% yield with 4 mols. HCl in MeOH, m. 175° (cor.). In PrOH and PhCH₃OH are formed large amts. of tarry material from which it is difficult to obtain pure products. C. A. R.

The so-called distyrenic acid of Fittig and Erdmann. R. STÖRMER and WALTER BECKER. *Ber.* 56B, 1440–8(1923).—F. and E.'s product, obtained by heating PhCH=CHCO₂H with moderately concd. H₂SO₄ (*Ann.* 216, 179(1882)), really consists of at least 3 different acids, 2 of which, C₁₇H₁₆O₃, designated *distyrenic* (I) and *distyrenic* (II) acid, are wholly satd., while the 3rd, for which the name *distyrenic acid* (III) is retained, is a mixt. of unsatd. substances which thus far has not been sepd. into its components.

II is shown to be a 1,2-diphenylcyclobutane-3-carboxylic acid (to which of the stereoisomeric forms of this acid II corresponds is as yet wholly uncertain), while to I, of which not enough was available for the detn. of its constitution, is provisionally assigned a 1,3-Ph₂ structure. The acid character and compn. of III indicate that it consists of a mixt. of acids of the types PhCH:CHCHPhCH₂CO₂H, CH₂:CPhCHPhCH₂CO₂H, PhCH:CHCH(CO₂H)CH₂Ph and CH₂:CPhCH(CO₂H)CH₂Ph or the other 8 possible isomers resulting from a change in the position of the double bond. The impossibility of hydrogenating these acids in the usual way indicates that they are not α,β -unsatd. compds. and their inability to form lactones that they are not β,γ -unsatd. compds. When freed from slight impurities, the originally soft substance gradually changes into a solid resinous mass, apparently a polymer of the original III; the increasingly difficult soly. in alkalis with time would indicate that the CO₂H group is involved in the polymerization. When P. and E.'s crude product (170 g. from 800 g. PhCH:CHCO₂H) is allowed to stand several months it begins to deposit crystals, m. 138°, which can be sepd., although with much loss, from the non-cryst. part by rubbing with ligroin, or better by esterifying the crude acid with Me₂SO₄-Na₂CO₃ and sapong. the fraction of the ester mixt. b₁₋₄ 170-80°. These crystals are apparently homogeneous and their m. p. does not change on recrystn. from various solvents, but by a tedious process of extn. with alc. at 0° they were sepd. into the rather difficultly sol. I (yield, 0.5% of the PhCH:CHCO₂H used), m. 176°, and the sol. II, m. 147°. Both I and II are stable towards Br and KMnO₄. Chloride of I, prepd. with SOCl₂ in C₆H₆, oil sensitive to moisture; amide, m. 215°; anilide, m. 194°; Me ester, prepd. with CH₂N₂, m. 53°. I is unchanged by heating with C₆H₅N at 160-70°, gives with KMnO₄, besides BzOH, only a small amt. of substance, m. 120°, which does not show the reactions of Bz₂. Chloride of II; amide, m. 205°; anilide, m. 198°; Me ester, prepd. with Me₂SO₄-Na₂CO₃, m. 72°. All attempts to rearrange II (heating with C₆H₅N at 160-70°, with fuming HCl at 150-60°, boiling 8 hrs. with 30% KOH, fusing 0.5 hr. with KOH) failed. All the salts of II are colorless (except the light green Cu salt), easily sol. in CHCl₃, CS₂ and Me₂CO and practically insol. in H₂O (except the K salt). With KMnO₄ in Na₂CO₃, II gives BzOH and Bz₂. The Ca salt, mixed with 2 parts soda-lime and distd. under 12 mm., gives a mixt. of the (stereoisomeric) PhCH:CPhEt as a pale yellow oil b₁₂ 162-7° and depositing crystals m. 56.5° (Klages and Heilmann, *Ber.* 12, 1975 (1879)). C. A. R.

Catalytic hydrogenation of liquids: cyclohexanol and hexahydrophenols. ANDRÉ BROCHET. *Chimie et industrie Special No.*, 587-95 (May 1923).—Mainly a review of B.'s work (see C. A. 8, 3180; 14, 946; 15, 907; 17, 271, 636, 916, 1004). The importance of agitation in the catalytic hydrogenation of liquids and solids is emphasized as the main difference between B.'s and Ipatiev's processes. A. PAPINEAU-COUTURE

The hydrogenation of phenol. JEAN DETRIE. *Chimie et industrie Special No.*, 596-601 (May 1923).—See Vavon and Detric, C. A. 15, 3287; Vavon, C. A. 15, 3780. A. PAPINEAU-COUTURE

Occurrence of l-menthone in pine oil. A. H. GILL. *Ind. Eng. Chem.* 15, 887 (1923).—Apinol, prepd. by dry distn. of pine wood, was redistd. and allowed to resinify for 14 yrs. The resulting oil (I) showed d_{15.4} 0.9856, n_D 1.4868, [α]_D -7° 20', and contained over 20% of l-menthone (II), b. 208.5-9.5°, and 8% dl-fenchyl alc., b. 202-3°. I was characterized by the absence of terpineol, and the presence of II, which heretofore has not been found in oils of the *Pinus* family. Large quantities of rosin oil were also present in I. LOUIS E. WISE

Rearrangement of carvone into carvacrol. FRIEDRICH RICHTER. *Chem.-Ztg.* 47, 489 (1923).—Repeated expts. failed to confirm the statement by Dormaar (cf. *Rec. trav. Chim.* 23, 394 (1904)) that heating at 205° serves to convert carvone into carvacrol without the aid of a catalyst, a claim in contradiction to the findings of Baeyer (cf. *Ber.* 27, 812 (1894)). W. O. E.

Caryophyllene. ERNST DEUSSEN. *Z. angew. Chem.* 36, 348-9 (1923).—After commenting on the results previously obtained with various co-workers on certain derivs. of α -, β - and γ -caryophyllene, brief reference is made to some recent work with Ober (*Diss. Leipzig*, 1923) on addn. compds. of caryophyllene (from clove oil) with Hg(OAc)₂, having the formula C₁₅H₂₄(HgOH)OAc(?) and reacting readily with KCl, KBr and KI, yielding compds. of the C₁₅H₂₄(HgOH)X form and well defined crystal habit but not giving the usual Hg tests. While this reaction fails in any sepn. of caryophyllene into its α - and β -forms, these addn. products appear nevertheless to be comparable to the active and inactive nitrosites of caryophyllene. W. O. E.

A sesquiterpene alcohol from elemi oil. H. JANSCH and P. FANTL. *Ber.* 56B, 1363-70 (1923); cf. Semmler, C. A. 12, 1190.—The solid compd. C₁₅H₂₄O found by several workers in the high-boiling fractions of elemi oil has now, by tedious mech. purification,

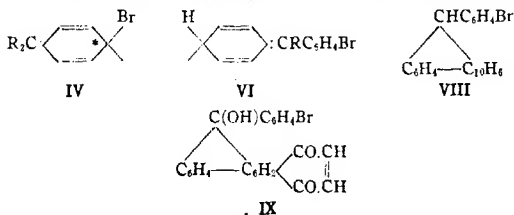
been isolated in cryst. form and is designated α -elemol (I); the results of the addn. of ICl and of catalytic hydrogenation with Pt, in connection with the optical consts. of I, indicate that it contains only 1 double bond and is therefore a bicyclic tertiary sesquiterpene alc. On benzylation it yields a liquid benzoate (II) which is hydrolyzed by alc. KOH to S's "elemol" (now designated β -elemol (III)), which has 2 double bonds and is therefore a monocyclic compd. This change is not brought about by the KOH in the hydrolysis of II, as I is unchanged when refluxed with KOH, but occurs during the benzylation, the mol. refraction of II showing that it, too, contains 2 double bonds. I b_{10} 142–3°, m. 46°, has a sharp pepper-like taste, mol. wt. in camphor 252, n_D^{20} 1.4273° (50 mm. tube), $n_D^{21.3}$ 1.49768, $d_{20.3}$ 0.94112. II, b_{10} 210 5°, n_D^{18} 1.5408, d_{18} 1.0346, decomps. with sepn. of BzOH when distd. several times *in vacuo*. III, b_{10} 143–4°, n_D^{18} 1.5070, d_{18} 0.9419. Refluxed with 1 mol. PhNCO, protected from moisture, I gives CO(NHPh)₂; heated 3 hrs. at 200° in a sealed tube with 3 parts Zn dust, it yields elemol, C₁₅H₂₄, b_{10} 115–9°, $n_D^{17.5}$ 1.4950, d_{17}^{17} 0.8830. With KMnO₄ or CrO₃-AcOH at room temp. are obtained only acid non-crystg. products isolated as the Ag salts, which, however, could not be sepd.; cold KMnO₄ decomps. the I completely. Dihydroelemol, from I in Et₂O with H and Pt sponge, b_{10} 150–1°, m. 46°. I has an I no. of 77 128 (calcd. for 1 double bond, 114.2). When it is treated in CHCl₃ with 1 mol. Br, the soln. immediately becomes intensely blue and no free Br or HBr can be detected; on distn. *in vacuo*, HBr and H₂O pass over after the CHCl₃ and 4 distns. yield a const. boiling emerald liquid, b_{10} 142°, with 68.18% C, 9.12% H and 20.99–21.03% Br. When I is sealed in a tube in colorless HNO₃ (d. 1.4) the acid becomes intensely red and after a time a violent reaction takes place with evolution of NO and formation of dinitrodihydrocinamic acid(?) (Dittmar, *Monatsh.* 25, 464), egg-yellow flocks easily sol. in alkalis with brown-red color, turns brown about 140°, sinters and decomps. above 155°. C. A. R.

Halogen acids as agents in the Beckmann rearrangement. FRITZ LEHMANN. *Z. angew. Chem.* 36, 360–2 (1923).—The recent work of Beckmann and Bark on Ph₂C:NOH (cf. C. A. 17, 3024) is discussed and new expts. are described involving the action of perfectly dry HCl, and in connection therewith also HBr and HI, on this oxime at about 110°, likewise the behavior of the halide salts of the oxime when heated to about 155°, showing in all cases more or less quant. rearrangement of the oxime to the anilide. The action of dry NH₃ on the oxime-HCl consisted on the other hand only in splitting off the HCl with formation of the free oxime; ultra-violet light had a similar effect. In all cases involving rearrangement of the oxime (or HCl salt) into PhNHCH₂Ph by HCl when subjected to heat, the entire mechanism consists first in the addn. of, second the splitting off of acid with simultaneous rearrangement of anilide. Such rearrangement as shown by L.'s expts. is fundamental for these changes, consisting as it does in the passage from a higher to a lower chem. potential. While various agents are capable of effecting the rearrangement of oxime to anilide, none has so far been found to bring about the reverse change. It is further shown that PhC(NO₂)H behaves like Ph₂C:NOH on treatment with dry HCl, yielding in this case PhNHAc. The behavior of α -benzil-monoxime, phenanthrenequinone monoxime-HCl and camphoroxime toward HCl and heat is briefly discussed. W. O. E.

The theory of variable affinity and its applications in organic chemistry. II. Application of the theory of variable affinity to diverse questions of organic chemistry. A. ORSKHOFF. *Rev. gen. sci.* 34, 292–305 (1923); cf. C. A. 17, 2863.—The theory previously developed is applied to various reactions of org. chemistry, including the formation and structure of the triarylmethyl and tetraarylhazirines, mol. transpositions in the α -glycol group and the halochromism of carbinols. Some facts contrary to the theory are also discussed. The original should be consulted for the theoretical discussion. JAMES BROWN

Triphenylmethyl. XXXIII. Quinoidation in the triarylmethyls. M. COMBERG AND F. F. BLICKE. *J. Am. Chem. Soc.* 45, 1765–79 (1923); cf. C. A. 17, 555.—Further evidence, of a strictly chem. nature, is advanced in favor of the view that color formation in the triarylmethyls must be ascribed not merely to the presence of a trivalent C atom but rather to the quinoidation of the free radical. This new evidence is based on a detailed study of *p*-BrC₆H₄CPH₂Cl (I), *p*-bromodiphenyl-*r*-naphthylcarbinol chloride (II) and diphenyl-4-bromo-*r*-naphthylcarbinol chloride (III), each of which contains a nuclear Br atom in the *p*-position to the methane C atom. It is possible, by treating the above chlorides with quite a large excess of very finely divided Ag for 20 min., completely to remove all the Cl and practically none of the Br; the free radicals were not isolated in cryst. form but their existence in the solns. was proved by the quant. absorption of O to form the peroxides, which were isolated and analyzed, and by the for-

mation of the iodides, R_2CI , with I. Further action of the Ag removes the nuclear Br, but only 50% of it under the most favorable conditions. This is explained by assuming that the Br is labile only in the quinonoid form (IV), in which the C^* atom to which the Br is attached has properties different from those in the original benzenoid form, $BrC_6H_4CR_2$ (V) or (VI). When a radical of type IV is produced, there undoubtedly exists, in addn. to a dynamic equil. between the unimol. forms IV, V and VI, an equil. between these and various bimol. forms. Such a bimol. form resulting from the union of V and V, VI and VI or V and VI would contain no labile Br, in that formed from IV and IV all the Br would be labile, while in that from IV and V or VI only 0.5 of the Br would be labile. Measurements of the amt. of O absorbed agree completely with these views; increase in the amt. of nuclear Br removed is paralleled by a decreased amt. of O absorbed by the product, and further confirmation has been afforded by isolation of the peroxides of these "radicals of the 2nd order" (VII), $BrC_6H_4CR_2C_6H_4CR_2$, as they are designated to distinguish them from the "radicals of the 1st order" (V). Again, as Cl is eliminated from II there results a blue-violet $KMnO_4$ -like soln. which gradually changes to an intense blue as the nuclear Br is removed. In the colorless salt-like derivs. of *p*-halogenated triarylcannabinols (chlorides, bromides, salts of org. acids), the nuclear halogen is not removed by Ag, while in the colored sulfates it is readily removed by Ag_2SO_4 ; it is assumed that the colorless sulfate formed by removing the Cl from I with Ag_2SO_4 immediately tautomerizes into the colored quinonoid sulfate from which the Ag_2SO_4 now removes the Br. *p*- $BrC_6H_4CPh_2OH$, prepd. from BrC_6H_4COPh or $BrC_6H_4CO_2Me$ with $PhMgBr$ and purified through I, m. $102-3^\circ$ (30° higher than given in the literature); I m. $112-4^\circ$. *p*-Bromodiphenyl-1-naphthylcarbinol, obtained in 80% yield from $C_{10}H_7MgBr$ and BrC_6H_4COPh , m. $132-3^\circ$, is turned intensely green by concd. H_2SO_4 or $HClO_4$; II m. $182-3^\circ$, forms intensely green addn. products with the chlorides of Zn, Sn, Fe, Hg and Al. The carbinol of II, heated with glacial AcOH and concd. H_2SO_4 , loses 1 mol. H_2O or HCl , giving *p*-bromophenyl-chrysofluorene (VIII) (6.1 g. from 10 g. of the carbinol), m. $233-5^\circ$, not colored by concd. H_2SO_4 ; 1.9 g. in AcOH with $Na_2Cr_2O_7$ gives 0.9 g. of the quinone IX, yellow, m. $172-3^\circ$; sol. in concd. H_2SO_4 with blood-red color, liberates I from alc. $KI-HCl$, is further oxidized by CrO_3 in AcOH to 2-[4- BrC_6H_4CO] $C_6H_4CO_2H$, m. $167-8^\circ$. *q*-Bromo-1-cyanonaphthalene, obtained in 80% yield by the Sandmeyer method from the NH_2 compd. diazotized with $AmNO_3$, m. $102-3^\circ$, is hydrolyzed by refluxing with $H_2O-AcOH-H_2SO_4$ to the CO_2H acid, m. $217-20^\circ$, whose *Et* ester, obtained in 90% yield with $EtOH-HCl$, m. $42-3^\circ$; this with $PhMgBr$ in $PhMe$ gives 60% diphenyl-1-bromo-1-naphthylcarbinol (purified through III), m. 130° ; III m. $160-1^\circ$, dissolves in concd. H_2SO_4 with deep green color. *p*-Bromodiphenyl-1-naphthylmethyl peroxide, m. 146° (decompn.), is colored deep green by H_2SO_4 . Peroxide of the radical of the 2nd order, $[BrC_6H_4(C_6H_5)CPhC_6H_4CPh(C_6H_5)]_2O_2$, cream-colored flocks, slowly begins to decomp. about 120° . Diphenyl-1-bromo-1-naphthylmethyl peroxide, darkens about 148° , m. $153-4^\circ$ (decompn.). Peroxide of the radical of the 2nd order, cream-colored amorphous substance, blackens about 135° and gradually melts with decompn., is colored deep green by H_2SO_4 . I, shaken in $PhNO_2$ with Ag_2SO_4 forms a red soln. of the quinonoid sulfate from which, after decolorizing by shaking with small amts. of 3% NaOH and acidifying the alk.



exts. with AcOH, is obtained *p*- $HOC_6H_4CPh_2OH$, m. $158-9^\circ$; from II is obtained $Ph(C_6H_7)C:C_6H_4O$, m. $168-70^\circ$ and from III $Ph_2C:C_6H_4O$, m. $178-9^\circ$. With Ag_2SO_4 , I gives, through the intermediate colored sulfite, 68% of $HOC_6H_4CPh_2OH$, while with $AgNO_3$ the product decomp. spontaneously and only picric acid is obtained.

C. A. R.

Action of ultra-violet light upon diketones. C. W. PORTER, H. C. RAMSPERGER AND CAROLYN STEEL. *J. Am. Chem. Soc.* 45, 1827-30(1923).— Bz_2 in dry C_6H_6 in a

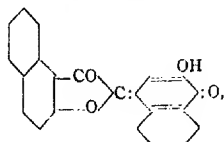
N atm. in quartz flasks exposed 1-7 hrs. at a distance of 20 cm. from a 220-v. Hg arc is unchanged. Bz_2 vapor (0.2755 g.) in an evacuated flask as 200° gave in 6 hrs. 18 cc. CO (0° , 760 mm.) and a corresponding amt. of Ph_2CO . Aq. solns. (50 cc. of a 0.03% soln.) exposed in the presence of air slowly became acid (1.94 cc. of 0.062 N $NaOH$ required for neutralization after 30 hrs.), the chief product being $BzOH$. In 66% alc. the Bz_2 was completely decompd. in 12 hrs., about 0.5 into an unidentified resinous product and the other 0.5 into $BzOH$, part of which was oxidized to $o-HOC_6H_4CO_2H$; in a N atm., $BzOH$ and benzoin, but no $HOC_6H_4CO_2H$, were formed. Benzoic acid in 50% alc. gives $(HOCPh_3)_2$ and, in the presence of air, Ph_2CO also. Ac_2 in H_2O gives $AcOH$ and AcH (153 cc. of 0.01 N $NaOH$ required for neutralization of 100 cc. of a 0.2% soln. after 10 hrs.); Ac_2 vapor (125 cc. at 100° under 1 atm.) evolves a gas (2 vols. CO and 1 vol. C_2H_4) at the rate of 8 cc. per min.

C. A. R.

Methylnaphthalene series. FRITZ MAYER AND OTTO SCHNECKO. *Ber.* 56B, 1408-15 (1923); cf. *C. A.* 17, 99.—In an attempt to synthesize $1,2-C_{10}H_8(CO_2H)_2$, $1,2-C_{10}H_7Me(NH_2)$ (I) was diazotized in dil. H_2SO_4 and treated with KI , giving 41% of 2-iodo-1-methylnaphthalene, b_{20} 196-9°, m. 53°, which with Mg in Et_2O and subsequent treatment with CO_2 yielded 40% 1-methyl-2-naphthoic acid, m. 178° (*Et ester*, b_{20} 190°, m. 27-8°), but all attempts to oxidize this acid (neutral or alk. $KMnO_4$, $K_2Fe(CN)_6$, HNO_3) failed. As a by-product in its formation was obtained 1,1'-dimethyl-2,2'-dinaphthyl, m. 227°. With Na in $AmOH$ I yields 5-methyl-6-aminonaphthalene 1,2,3,4-tetrahydride, b_{20} 170-5°, does not absorb CO_2 from the air, can be diazotized and coupled with β -naphthol to a deep red dye; *Ac deriv.*, m. 134°; *Bz deriv.*, m. 222°; *HCl salt*, m. 263-4°. Di- β -naphtholmethane, the starting point in the above syntheses, heated 60 hrs. at 150-60° with 40% aq. $(NH_4)_2SO_4$ and 20% NH_4OH gives 1,2,1',2'-dinaphthacridine, m. 216°, while if the temp. is kept at 110-20° the product is 2-amino-2'-hydroxydi-1,1'-naphthylmethane, m. 121°; *Ac deriv.*, m. 132°; *Bz deriv.*, m. 150°. Di- β -[naphthyl-2-]propionate, obtained by esterification of the acid, b_{20} 195-8°; refluxed 4 hrs. in alc. with NH_4H_2O it gives 88% of the hydrazide, m. 156°, which in a little cold HCl with $NaNO_2$ yields the azide and this with alc. gives the urethan, m. 83°; hydrolyzed by boiling 20 hrs. with alc. KOH to $2-C_{10}H_7CH_2CH_2NH_2$ (II), b_{20} 174-5°; *Bz deriv.*, m. 140-1°; *picrate*, yellow, m. 196°. II is also obtained in 60% yield from $2-C_{10}H_7CH_2Br$ and $NaCN$ in hot aq. alc., followed by reduction of the resulting cyanide (b_{20} 202-5°, m. 86°), which is obtained in 80% yield, in tetralin with a Ni catalyst and H under 25 atm. below 105° ; as by-product is obtained 3-6% of the sec. bis- β -[naphthyl-2-]ethylamine (which is obtained in 20% yield if the reduction is carried out at 120°), b_{20} 270-80°, m. 87°; *NO deriv.*, m. 179°; forms a blue soln. when heated with an equal wt. of $PhOH$ in 1:1 H_2SO_4 until a red color results, dild. with H_2O and made alk.; *picrate*, yellow, m. 138-9°; *HCl salt*, m. 289°. $1-C_{10}H_7CH_2CH_2NH_2$ (III), similarly obtained in 30% yield from $1-C_{10}H_7CH_2Br$ at 110° , b_{20} 182-3°; *picrate*, yellow, m. 201-2°; *Bz deriv.*, softens 87°, m. 97°. Bis- β -[naphthyl-1-]ethylamine, viscous liquid, b_{20} above 320° ; *picrate*, m. 179°; *NO deriv.*, m. 114-5°, gives the Liebermann reaction; *HCl salt*, m. 222°. II (8.5 g.) in 20 cc. $AcOH$ and 7 cc. concd. HCl allowed to stand 1-2 hrs. on the H_2O bath with 3.7 g. $HCl(OMe)_2$ gives about 1 g. 3,4-(naphtho-1',2')-pyridine 1,2,3,4-tetrahydride (IV), b_{20} 200-5°, m. 40°, absorbs CO_2 from the air. It is also obtained by heating in concd. HCl the anhydrolform- β -[naphthyl-2-]ethylamine, m. 117°, which results in 80% yield from II in Et_2O and 30% $HCHO$. *Picrate* of IV, m. 225-6°; dithiocarbamate, m. 192°; *NO deriv.*, m. 105°, gives the Liebermann reaction; *HCl salt*, m. 275-6°; carbonate, begins to decomp. 124° ; *o-nitrobenzoyl deriv.*, m. 240°. When IV is oxidized with alk. $KMnO_4$ and the resulting brown oil is heated at 190-200° with a mixt. of 3 cc. fuming HNO_3 and 2 cc. H_2O , $1,2,3,4-C_{10}H_6(CO_2H)_4$, m. 237°, is obtained.

C. A. R.

Autoxidation of 1-aceto-2-naphthol. K. FRIES AND H. JÜHLERS. *Ber.* 56B, 1304-8 (1923); cf. *C. A.* 16, 3085.— $1,2-C_{10}H_7Ac(OH)$ (I) undergoes in alk. soln. an auto-oxidation entirely analogous to that of the 2,1-isomer, yielding 2-[4,5-benzocoumarone]-1'-[3'-hydroxynaphthalene]indolignone (II),



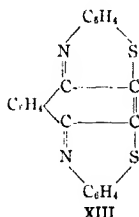
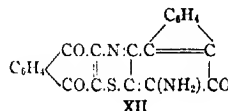
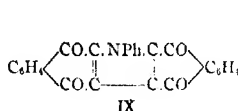
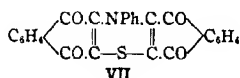
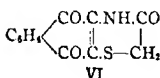
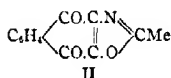
which differs from its isomer only in that its methylation is much more difficult and that acetylation with Ac_2O gives a *triacetate* (III) which on gentle warming yields the *monoacetate* (IV). I, m. 60° , is obtained in 60% yield from $\beta\text{-C}_{10}\text{H}_7\text{OAc}$ heated with AlCl_3 at 120° ; 18.6 g. in 4 g. NaOH and 120 cc. H_2O evapd. to dryness in a flat dish on the H_2O bath, taken up in H_2O and again evapd. gives 3 g. II, bright red, darkens 260° , m., 308° , dissolves in concd. H_2SO_4 with blue-green color, reprecipitated unchanged by H_2O , forms with alkalis black, almost insol. salts sol. in alc. with deep blue color and hydrolyzed on diln. with H_2O ; boiled 2 min. in 5 parts PhNH_2 it decomps. into 4,5-benzo-3-coumaranone (V) and β -anilinnaphthoquinone; *carboxy deriv.*, from II, rubbed with alc. and shaken in excess of dil NaOH with ClCO_2Et , red-brown, m. 243° , hydrolyzed by alc. NaOH to the Na salts of II. II can be synthesized by boiling a concd. soln. of equal parts V and 2-hydroxy-1,4-naphthoquinone-4-anil in AcOH 0.5 hr. or by boiling 0.5 g. β -naphthoquinone and 0.6 g. V 3 hrs. in alc. (yield 10%). V, m. 133° , is obtained in 30-5% yield by slowly treating $\beta\text{-C}_{10}\text{H}_7\text{OCH}_2\text{CO}_2\text{H}$ in C_6H_6 suspension with PCl_5 , heating on the H_2O bath until the evolution of HCl ceases, cooling with ice, slowly adding 36 g. AlCl_3 and heating 3 hrs. on the H_2O bath. III m. 223° , 4,2,1- $\text{C}_{10}\text{H}_6\text{BrAc}$ (OH) is stable towards air in alk. soln. and PhO in boiling AcOH or C_6H_6 ; with HNO_3 (d. 1.6) below 40° it gives 4,2,1- $\text{C}_{10}\text{H}_6(\text{NO}_2)\text{Ac}$ (OH), m. 159° . Under the same conditions, 4,2,1- $\text{C}_{10}\text{H}_6\text{BrEt}$ (OH) gave 2-ethyl-1,4-naphthoquinone. C. A. R.

Hydrogenation of aromatic compounds with the aid of platinum. VI. Hydrogenation of naphthalene. RICHARD WILLSTÄTTER AND FRANZ SEITZ. *Ber.* 56B, 1388-407 (1923); cf. C. A. 15, 3830.—It has been found that hydrogenation of C_{10}H_8 with Pt sponge yields decahydronaphthalene (I) directly without passing through any intermediate product (tetrahydronaphthalene (II)) (C. A. 7, 1508) while the Sabatier-Senderens Ni method and the Schroeter com. process first give II. In attempting to repeat the earlier work it was found that often I could not be obtained and that pure II was formed. This contradiction has been found to be due to the O content of the Pt sponge and the H. The relative velocities of the 3 possible reactions involved in the hydrogenation of $\text{C}_{10}\text{H}_8(\text{C}_{10}\text{H}_8 \rightarrow \text{II}, \text{II} \rightarrow \text{I}, \text{C}_{10}\text{H}_8 \rightarrow \text{I})$ were detd. by studying the hydrogenation of mixts. of C_{10}H_8 and II. If such mixts. are treated with just enough H to convert the C_{10}H_8 into II, the resulting product will contain C_{10}H_8 and I in the mol. ratio 3:2, with varying amts. of II. Refractometric measurements on such ternary mixts. showed that n is a linear function of the concn. of II so that a single detn. of n of such a mixt. is sufficient to det. its compn. The hydrogenations were carried out in AcOH . The C_{10}H_8 , freed from 8 compds. by the method earlier described and crystd. twice each from AcOH and Me_2CO and 3 times from alc., showed $n_D^{25.0} 1.58987$. The II, purified through the SO_3H acid, $b_{718.3} 204.0-4.5^\circ$, $d_{4.0}^{20.0} 0.9712$, $n_D^{20.0} 1.5428$. The I $b_{713.4} 188.0-9.0^\circ$, $d_{4.0}^{20.0} 0.8942$, $n_D^{20.0} 1.4795$. The results of the numerous measurements, which are reported in detail, show that C_{10}H_8 is reduced to II or directly to I, II being formed chiefly with Pt sponge rich in O (Reaction 1) and I, without any detectable intermediate product, with a catalyst poor in O (Reaction 2). It is probable that II is also formed chiefly with Pt and H poorest in O (Reaction 3), (3) being the slowest reaction of the 3 and (1) the most rapid. The simplest explanation is that the hydrogenation proceeds through various dihydronaphthalenes (probably 3), that in (1) being the most stable and the one in (3) the least stable; the former is probably the Δ^1 , the latter the Δ^2 -compd., and the one formed in (2) the 1,5-compd. C. A. R.

New (observations) on 2,3-dichloro-1,4-naphthoquinone. K. FRIES AND P. OCHWAT. *Ber.* 56B, 1231-304 (1923).—2-Acetyl-3-chloro-1,4-naphthoquinone, from the NH_2 compd. (I) rubbed with cold Ac_2O and a few drops concd. H_2SO_4 , brown-red leaflets rubbing to a yellow powder, m. 219° , converted by boiling NaOH into hydroxy-chloronaphthoquinone. 2-Methyl-1,4-naphthoxazole-4,9-quinone (II), from I boiled 0.5 hr. with Ac_2O and a few drops concd. H_2SO_4 , brownish yellow, m. 317° ; short warming with concd. H_2SO_4 or with dil. NaOH and alc. ruptures the oxazole ring with formation of aminohydroxynaphthoquinone (III) but boiling alkali evolves NH_3 ; boiled in Ac_2O with Zn dust until the soln. is almost colorless, it gives 2-methyl-4,9-diacetoxy-1,4-naphthoxazole (IV), m. 222° , converted into III by hot alkalis. 2-Amino-3-methylmercapto-1,4-naphthoquinone, from I boiled in alc. with Na_2S until it dissolves and then warmed with a slight excess of Me_2SO_4 , brown-red, m. 132° , sol. in concd. H_2SO_4 with brown-red, in alc. alkalis with wine-red color; attempts to convert it into the sulfoxide failed, H_2O_2 splitting off the SMe group, even when an excess is avoided. The corresponding anilino compd. (C. A. 16, 2471) behaves in the same way towards H_2O_2 , giving 2-anilino-1,4-naphthoquinone, m. 193° . When $\text{ClCH}_2\text{CO}_2\text{Na}$ is used instead of Me_2SO_4 in the above reaction the product is 2-amino-3-thioglycolic acid-1,4-naphtho-

quinone (V), brown, m. 220° (decompn.), sol. in alkalis with brown color (yield, 90%); boiled 0.5 hr. in AcOH it gives 90% of 2,3-dihydro-3-keto-*lin-naphtho-p-thiazine-5,10-quinone* (VI), dark brown, m. 260° (decompn.), sol. in NaOH with cleavage into V, converted by Zn dust in hot Ac₂O into the 5,10-diacetoxithiazine, m. 270° (decompn.), which is converted by hot NaOH under the action of the air into V. 1,4-Phenyl-*lin-dinaphtho-p-thiazine-1,6,7,12-diquinone* (VII), from 2-amino-3-chloro-1,4-naphthoquinone boiled 15 min. with Na₂S in aq. alc. and then 1 hr. with 2,3-dichloro-1,4-naphthoquinone (VIII), brown crystals difficultly sol. in the ordinary solvents, dissolves in H₂SO₄ with brown color, is not attacked by aq. alkalis, decomp. in boiling PhNO₂, more rapidly when heated in AcOH suspension with a little HNO₃ (d. 1.4), into 1,3-phenyl-*lin-dibenzocarbazole-1,6,7,12-quinone* (IX), yellow, m. above 400°, stable towards hot HNO₃, unattacked by alkalis, sol. in H₂SO₄ with yellow color, gives in hot Ac₂O suspension with Zn dust the 1,6,7,12-tetracetoxycarbazole (X), yellow, m. 275° (decompn.), shows in soln. blue-yellow fluorescence changing to green-yellow on addn. of alkalis, regenerates IX with hot H₂SO₄. Heated several hrs. on the H₂O bath with excess of SnCl₄-AcOH IX gives the 1,6-monoquinone (XI), deep brown, m. above 360°, shows faint greenish yellow fluorescence in soln. 2-*p*-Chloroanilino-3-chloro-1,4-naphthoquinone, from *p*-ClC₆H₄NH₂ and VIII, red, m. 266°. 1,4-*p*-Chlorophenyl analog of VII, brown, m. above 360°; of IX, yellow, m. above 360°; of X, yellow, m. above 360°; of XI, brown, m. above 360°, forms a brown Na₂S₂O₄ vat turned green by air and reprecip. the original quinone with more air. 2,3-Diazido-1,4-naphthoquinone, from VIII in alc. suspension heated a few min. on the H₂O bath with concd. aq. NaN₃, orange, m. 136°, not sensitive to rubbing or shock, deflagrates on rapid heating above the m. p., at 100° in *vacuo*, decomp. explosively on addn. of a drop of concd. H₂SO₄. 2-Acetoxy-3-chloro-1,4-naphthoquinone, from VIII in alc. suspension heated with NaOAc, yellow, m. 98°, hydrolyzed by alkalis to the 2-HO compd. The compd. XII, from 2-amino-3-mercapto-1,4-naphthoquinone (prepd. by boiling I in alc. suspension with Na₂S) boiled 1 hr. with I, brownish yellow, m. above 360°, very stable towards alkalis, sol. in H₂SO₄ with brown color. *o*-O₂NC₆H₄NH₂, β -C₆H₄(CO)₂C₆H₄NH₂ and I do not react with VIII under the most varied conditions (heating in alc.; in the presence of *Naturkaffee C*, ZnCl₂, NaOAc, NaOEt, C₆H₅N; in xylene, PhNO₂ or quinoline as solvents; on fusing the components together). Attempts to condense VIII with C₆H₆ in the presence of AlCl₃ failed. 2,3-Bis-*o*-nitrophenylmercapto-1,4-naphthoquinone (XII), from VIII heated 0.5 hr. with 2 mols. O₂NC₆H₄SH in alc., cinabar-red, m. 253°, unattacked by alkalis, sol. in concd. H₂SO₄ with deep brown-red color and reprecip. unchanged by H₂O, converted by rubbing with 4 parts AcOH and adding 2 parts SnCl₄-AcOH (1:3) into the 1,1-dihydroxy-*naphthalene*, m. 233°, which is oxidized back to XII on soln. in concd. H₂SO₄ and yields a diacetate, m. 217°. When 10 g. XII suspended in 10 cc. AcOH is heated with 80 cc. SnCl₄-AcOH (1:3) until the hydroquinol first formed has dissolved, it yields the SnCl₄ double salt, needles with black surface luster, of 1,2,3,4-dibenzonaphthodithiazine quinone diimide (XIII), deep red, m. above 360°; its salts dissolve with deep green color and are reduced by Zn dust in AcOH to a greenish yellow cryst. substance, probably the *d*-thiazine, which is quickly oxidized back to XIII by the air. 2-*o*-Nitrophenylmercapto-3-anilino-1,4-naphthoquinone, from XII boiled a short time with PhNH₂, blue-red leaflets with blue-violet surface luster, m. 216°, sol. in dil. NaOH at room temp. with deep brown color, acids pptg. a bright red product. Tetra-*o*-nitrophenylmercapto-1,4-benzoquinone (XIV), from 2.46 g. chloranil (XV) in boiling alc. with 6.2 g. O₂NC₆H₄SH, brownish yellow, deflagrates violently on heating, attacked only with difficulty by alc. KOH and concd. H₂SO₄, changes on long boiling in PhNO₂ into a distinctly colored product of the same empirical compn. but difficultly sol. in PhNO₂, sol. in PhNH₂ with replacement of 2 of the O₂NC₆H₄S groups by PhNH residues. The only product which could be isolated pure in relatively good yield from the product of the action of 2 mols. O₂NC₆H₄SH on XV had the compn. of a chlorotris-*o*-phenylmercaptobenzoquinone. 2,5-Dianilino-3,6-bis-*o*-nitrophenylmercapto-1,4-benzoquinone, from XIV boiled a few min. in PhNH₂, bright yellow-red, m. above 360°, easily sol. in dil. alc. KOH, reprecip. unchanged by acids, sol. in H₂SO₄ with dark violet color. 2,5-Dichloro-3,6-diazido-1,4-benzoquinone (XVI) (1.8 g. from 2.4 g. XV in AcOH with 2.6 g. NaN₃ in concd. aq. soln.), cinabar-red, sol. in xylene but not without decompn., deflagrates very violently on heating, is not sensitive to shock, smoothly converted in alc. suspension by slowly adding cold aq. Na₂S to the 3,6-(NH₂)₂ compd., whereas if it is added to the Na₂S and warmed a few min. on the H₂O bath NH₃ is liberated and Na chloraurate seps. on cooling. Heated with PhNH₂ it gives chiefly the 3,6-(PhNH)₂ compd. which does not react with NaN₃. Tetrazido-1,4-benzoquinone, from XVI in alc. suspension cautiously warmed with excess of NaN₃, brownish yellow crystals with blue-black surface luster, difficultly sol.

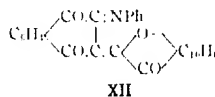
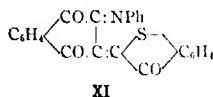
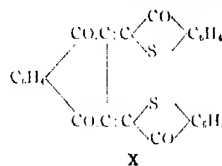
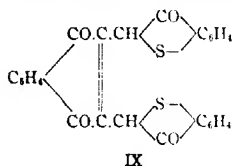
in alc. and decompd. by it on warming, is extraordinarily explosive when heated on Pt foil, rubbed or struck, evolves N on attempted soln. or on treatment with Na_2S .



C. A. R.

Indigoid compounds from 2-hydroxy-1,4-naphthoquinone-4-anil and benzocoumaranones or hydroxythionaphthene. K. FRIES AND H. EHLERS. *Ber.* 56B, 1308-19(1923); cf. preceding abstr.—In the synthetic prepn. from benzocoumaranones and 2-hydroxy-1,4-naphthoquinone-4-anil (I) of the red compds. $\text{C}_{27}\text{H}_{20}\text{O}_4$ obtained by the autoxidation in alk. soln. of the $\text{C}_{17}\text{H}_{14}\text{Ac}(\text{OH})$ there are always formed small amts. of a blue and a green compd. and the same thing has been found to occur in the action of 3-hydroxythionaphthene (II) on I. Now, the Me ether, acetate and carboxy deriv. of I, and even I itself, decomp. on heating in soln., forming as I of the products 2-anilino-1,4-naphthoquinone-4-anil (III) and the blue by-product obtained in the reaction between II and I in AcOH is 2-thionaphthene-1'-[3'-anilinonaphthalene]-indolignone (IV), which is easily obtained from III and II. When the condensation between I and II is carried out in alc. instead of AcOH, H_2O , not PhNH_2 , is eliminated and the product is the red 2-thionaphthene-1'-[2'-hydroxynaphthalene]indolignone-4'-anil (V), while II with the Me ether of I gives a 3rd, blue-green isomer, 2-thionaphthene-2'-[4'-anilinonaphthalene]indigo (VI), MeOH being split off. With the coumaranones instead of II the results are in general the same. II (1.5 g.) boiled 10 min. in AcOH with 2.5 g. I gives as chief product (0.15 g.) 2-thionaphthene-1'-[3'-hydroxynaphthalene]-indolignone (VII), red, m. 224° , also obtained in alc. with HCl but with no better yields. V, from II, 2 parts I, 50 parts alc. and 5 parts Ac_2O boiled 5 hrs. (yield, 20%), dark red, m. 242° , not attacked by aq. NaOH but dissolves in alc. with dark blue color and is reprecipitated unchanged by acids, dissolves in concd. H_2SO_4 with dirty brown color, rapidly decomps. in boiling PhNO_2 (especially in the presence of moisture) with formation of thioindigo. The crude product contains a little of the isomeric IV, deep blue, m. 234° which is obtained in 0.9 g. yield from 2.1 g. III and 1 g. II boiled 1 hr. in AcOH; it dissolves in H_2SO_4 with deep green color, is not attacked by cold NaOH, is decompd. by hot alc. KOH and by mineral acids in boiling AcOH into VII; conversely, VII with PhNH_2 and ZnCl_2 in boiling alc. gives IV. The Me ether of I is obtained in 80-5% yield from I and alk. Me_2SO_4 ; boiled 5 min. in AcOH with II, it gives 20% of VI, green-blue needles, often with a bronze luster, m. about 224° (decompn.), sol. in NaOH contg. a few drops of alc. with green color, reprecipitated unchanged by acids, sol. in H_2SO_4 with light green color; the crude product contains some IV. Boiled 3 hrs. with PhNH_2 , VI yields III. With boiling $\text{Ac}_2\text{O-NaOAc}$, IV gives 2-[3-acetoxythionaphthene]-1,4-naphthoquinone-4-anil, bright red, m. 174° , sol., with hydrolysis, in H_2SO_4 with green color, also easily hydrolyzed by boiling alc. KOH. 2-[5-bromo-6,7-benzocoumarone]-1'-[3'-hydroxynaphthalene]indolignone, from 5-bromo-6,7-benzo-3-coumaranone and I in boiling AcOH, red, begins to darken 285° , m. 310° (decompn.), also obtained from the

coumaranone and β -naphthoquinone in boiling alc. 2-[4,5-Benzocoumarone]-1'-[3'-anilinonaphthalene]indolignone, from the coumaranone and III, blue, m. 280° (decompn.) stable towards both alc. alkalies and mineral acids. 2-[5-Bromo-6,7-benzocoumarone]-1'-[3'-anilinonaphthalene]indolignone, from the bromocoumaranone and III, blue needles with bronze luster, m. 270° (decompn.), does not split off the PhNH group with hot alc. KOH or mineral acids in AcOH. 2-[4,5-Benzocoumarone]-2'-[4'-anilinonaphthalene]indigo (3 g. from 5 g. of coumarone and the Me ether of I), dark green, m. about 280° (decompn.), sol. in hot H₂SO₄ with pure blue color, reprecipitated unchanged by H₂O, quite stable towards alc. KOH and forms no Ac deriv. with Ac₂O-AcONa. 2-[5-Bromo-6,7-benzocoumarone]-2'-[4'-anilinonaphthalene]indigo, green, carbonizes 232°. 2,3-Dichloro-1,4-naphthoquinone (VIII) (2.27 g. and 2 mols. II in boiling alc. give 1.8 g. of a compd. IX, almost black, rubs to a red-violet powder, m. above 360°, sol. in PhNO₂ with deep reddish violet color, hardly attacked by concd. H₂SO₄ and aq. or alc. KOH, forms a dark green Na₂S₂O₄ vat, from which it is reprecipitated by air. 4,5-Benzo-2-coumaranone and VIII similarly yield a compd. X, dark violet, m. above 360°, difficultly sol. in H₂SO₄ with green color, forms a dark vat. Compd. XI, from 2-chloro-3-anilino-1,4-naphthoquinone and II, dark red, m. above 360°, sol. in H₂SO₄ with orange red, in alc. KOH with deep blue color, reprecipitated unchanged from both solvents by H₂O. Compd. XII, from 2-chloro-3-anilino-1,4-naphthoquinone and 4,5-benzo-2-coumaranone, bright red, m. above 360°, sol. in H₂SO₄ with yellow-red, in alc. NaOH with red-violet color.



(F. and E. seem to use the names 2- and 3-hydroxy 1,4-naphthoquinone-4-anil indiscriminately for the same compd.—ABSTR.) C. A. R.

Naphthalene hydrides and their uses. CH. LORMAND. *Chimie et industrie*, Special No., 602-6 (May, 1923).—A description of the prepn. of tetralin and of its com. uses. A. PAPINEAU-COUTURE

Formation of six-membered carbon rings. FRITZ MAYER AND GEORG STAMM. *Ber.* 56B, 1424-33 (1923); cf. C. A. 17, 99. It was found in the earlier work that the yields of cyclic compds. obtained from 1- and 2-C₁₀H₇CH₂CH₂COCl under the influence of AlCl₃ are considerably poorer than that from C₁₀H₇CH₂CH₂CH₂COCl. The present work was undertaken to det. whether branching of the chain in general increases the yield of cyclic compd. formed from this chain and also whether nucleus alkylation of the aromatic residue likewise favors the ring formation. A study of γ -phenyl- and γ -*p*-tolylbutyryl chlorides and of their α -, β - and γ -Me derivs. showed that such is the case, the yields of cyclic compd. from the Me derivs. (including MeC₆H₄CH₂CH₂CH₂COCl) being 70-6% and that from Ph(CH₂)₃COCl only 10%. Methylsuccinic acid is obtained in 65% yield from citraconic anhydride in H₂O with PdCl₂, animal charcoal and H under 1.6 atm. excess pressure; refluxed 1 hr. with AcCl it gives 80.5% of the anhydride (I), b₁₆ 120-2°. The Ph(CH₂)₃COCl was prepd. by reducing BzCH₂CH₂CO₂Et by the Clemmensen method, saponig. and allowing the resulting acid to stand 1 day with 3 parts SOCl₂; 14.5 g. with AlCl₃ gives 1.2 g. α -tetralone, b₁₄ 133-5° (semicarbazone, m. 216-7°). 7-Methyl-1-ketonaphthalene 1,2,3,4-tetrahydride (11.5 g. from 20 g. *p*-MeC₆H₄(CH₂)₃COCl), b₁₄ 143-5°, m. 35-6°; semicarbazone, m. 226-8°. Oppenheim (*Ber.* 34, 4228 (1901)) and Krollpfeiffer and Schäfer (C. A. 17, 2422) overlooked the fact that I condenses with C₆H₆ and PhMe in 2 ways; heated 3 hrs. at about 40° with 5 parts C₆H₆ it gives about 75% BzCH₂CHMeCO₂H, m. 139-40°, while the mother liquors on concn. yield a small amt. of the isomeric β -benzoyl β -methylpropionic acid, m. 56-6°. 2-Methyl-1-ketonaphthalene 1,2,3,4-tetrahydride (2.35 g. from 4.1 g. PhCH₂CH₂CHMeCOCl), b₁₄ 135-7°. From 20 g. I with AlCl₃ in PhMe are similarly

obtained 10.5 g. β -*p*-toluyl- α -methylpropionic acid, m. 169-71° (oxime, m. 141-2°), and 15 g. of the β -*Me* isomer, m. 63-5° (oxime, m. 139-41°); both acids with $\text{HNO}_3 \cdot \text{H}_2\text{O}$ at 150-70° give $p\text{-C}_6\text{H}_4(\text{CO}_2\text{Me})_2$. The α -*Me* acid was also prepd. from $p\text{-MeC}_6\text{H}_4\text{COCH}_2\text{Br}$, $\text{MeCH}(\text{CO}_2\text{Et})_2$ and NaOEt . γ -*p*-Tolyl- α -methylbutyric acid, b_{15} 183-4°, m. 54-5°; *Et* ester, b_{15} 149-51°; chloride, b_{15} 145-6°; amide, m. 150-1°; 12 g. of the chloride yield 7.5 g. of 2,7-dimethyl-1-ketonaphthalene 1,2,3,4-tetrahydride, b_{15} 145-7°; semicarbazone, m. 220-1°. β -*Me* acid, b_{15} 180-1°; *Et* ester, b_{15} 149-51°; chloride, b_{15} 141-3°; 3,7-dimethyl tetrahydride (3.7 g. from 6.2 g. of the chloride), b_{15} 150°, m. 52-3° (semicarbazone, m. 203-5°). γ -Phenyl- γ -methylvinylacetic acid (7.3 g. from 33 g. $\text{BzCH}_2\text{CH}_2\text{CO}_2\text{Et}$ with MeMgI), m. 75-8°; 6 g. reduced, as the Na salt, with H, PdCl_2 and charcoal gives 6 g. γ -Phenyl- γ -methylbutyric acid, b_{15} 169-70°; 4 g. of the chloride of this with AlCl_3 in petr. ether yields 2.3 g. 4-methyl-1-ketonaphthalene 1,2,3,4-tetrahydride, b_{15} 145-60°; semicarbazone, m. 210°. $\text{Me}(p\text{-MeC}_6\text{H}_4)\text{CHCH}_2\text{CH}_2\text{CO}_2\text{H}$ (7.5 g. from 8 g. $\text{Me}(\text{MeC}_6\text{H}_4)\text{C} \cdot \text{CHCH}_2\text{CO}_2\text{H}$), b_{15} 178-80°; chloride, b_{15} 145-55°; 7 g. of the latter with AlCl_3 yields 4.4 g. of 4,7-dimethyl-1-ketonaphthalene 1,2,3,4-tetrahydride, b_{15} 145-52°; semicarbazone, m. 194-5°. Repetition of v. Pechmann's work (Ber. 15, 891(1882)) showed that 25 g. citraconic anhydride in C_6H_6 with AlCl_3 yields 0.3 g. β -benzoyl- α -methylacrylic acid, softens 120°, m. 150°, reduced with charcoal and PdCl_2 to $\text{BzCH}_2\text{CHMeCO}_2\text{H}$, and 0.2 g. of the β -*Me* isomer, softens 80°, m. 100-2°, whose reduction yields an acid which could not be made to solidify. Similarly, from 10 g. of the anhydride in PhMe are obtained 2.5 g. β -*p*-toluyl- α -methylpropionic acid, m. 138-9°, reduced to $\text{MeC}_6\text{H}_4\text{COCH}_2\text{CHMeCO}_2\text{H}$, and the β -*Me* isomer, m. 94-5°, reduced to $\text{Me}(\text{MeC}_6\text{H}_4)\text{COCHCH}_2\text{CO}_2\text{H}$. C. A. R.

Derivatives of anthraquinone. Reactions of anthraquinonesulfonic acids with mercaptans. W. S. HOFFMAN and E. E. REID. *J. Am. Chem. Soc.* 45, 1831-8(1923).—This work was undertaken to det. the best conditions under which SO_3H groups in the α -positions in anthraquinone can be replaced by mercaptan residues (C. A. 16, 256) and to extend the reaction to other mercaptans than those already studied. PhCH_2SH works well, yielding well characterized derivs. $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{SH}$ reacts rapidly but the products are complex, very slightly sol. and difficult to handle. *iso*- PrSH easily gives good yields of characteristic products but the corresponding sulfones are obtained in small yield, if at all, since the *iso*- Pr group is readily oxidized to SO_2H and the SO_3H acids are obtained quant. if the oxidation is vigorous. $\text{HSCH}_2\text{CH}_2\text{OH}$ reacts normally. $(\text{CH}_3\text{SH})_2$ reacts rapidly but the products are complicated and could not be purified. $1,5\text{-BuSO}_2\text{C}_6\text{H}_3(\text{CO})_2\text{C}_6\text{H}_3\text{SO}_2\text{Na}$ (I) reacts extremely rapidly with mercaptans in hot alk. soln., immediately giving a ppt. of the thioether $\text{BuSO}_2\text{C}_6\text{H}_3\text{O}_2\text{SR}$; the yields are practically quant. and the reaction may advantageously be used for the identification of mercaptans; although the m. ps. of these products are definite, it is better, however, to oxidize with fuming HNO_3 to the mixed disulfones, which are particularly easy to purify and have good m. ps. I also reacts with PhSH at a satisfactory rate. A study of the influence of time, diln. and amt. of alkali in the prepn. of $\text{C}_6\text{H}_3(\text{CO})_2\text{C}_6\text{H}_3\text{SBu}$ showed that the best yield (86%) from 1 part of the $\text{C}_6\text{H}_3(\text{CO})_2\text{C}_6\text{H}_3\text{SO}_2\text{Na}$ and 1.25 mols. BuSH is obtained in 25 parts H_2O with 4 mols. NaOH after 4 hrs. boiling. The following compds. were prepd.: *Benzylanthraquinone thioethers*: 1-mono, m. 242°, golden yellow; 1,5-di-, m. 176° dull orange; 1,8-di-, m. 189°. *Na* 1,5- and 1,8-benzylmercaptanthraquinonesulfonates, contain 2 and 3 mols. H_2O , resp. *Alkyl benzyl anthraquinone dithioethers* (m. p. and color of the 1,5- and 1,8-derivs., resp.): *Me*, 276°, golden; 262°, crimson. *Et*, 208°, orange; 164°, orange. *Pr*, 210°, orange; 181°, orange. *Bu*, 235°, orange-yellow; 185°, orange-red. *iso*-*Pr*, 239°, orange; 229°, orange-red. *iso*-*Am*, 211°, orange; 189°, orange-red. *Benzyl anthraquinone 1-sulfone*, m. 233°; *dibenzyl 1,8-disulfone*, m. 202°. *Alkyl benzyl anthraquinone disulfones* (m. ps. of the 1,5- and 1,8-derivs., resp.): *Me*, 280°, 255°; *Et*, 210°, 242.5°; *Pr*, 215°, 227°; *Bu*, 228°, 210°; *iso*-*Pr*, 229°. —; *iso*-*Am*, 202°, 201°. *Isopropyl anthraquinone thioethers*: 1-mono, m. 134°; golden; 1,5-di-, m. 148°, orange; 1,8-di-, m. 181°, orange-red. *Na* 1,5- and 1,8-isopropylmercaptanthraquinonesulfonates, contain 2 and 3 mols. H_2O , resp. *Alkyl isopropyl anthraquinone dithioethers* (m. ps. and colors of the 1,5- and 1,8-derivs.): *Me*, 184°, orange; 189°, crimson. *Et*, 163°, golden; 176°, crimson. *Pr*, 133°, golden; 135°, orange-red. *Bu*, 114°, orange-yellow; 131°, orange-red. *iso*-*Am*, 97°, brownish; 109°, orange-red. With fuming HNO_3 the 1- $\text{MeCHSC}_6\text{H}_3(\text{CO})_2\text{C}_6\text{H}_3$ gives 81% of 1- $\text{C}_6\text{H}_3(\text{CO})_2\text{C}_6\text{H}_3\text{SO}_3\text{H}$ and only a small amt. of $\text{C}_6\text{H}_3(\text{CO})_2\text{C}_6\text{H}_3\text{SO}_2\text{CHMe}_2$, m. 182°; the mixed 1,5-diethers contg. an *iso*- Pr group give 80-85% of the alkylsulfonesulfonic acid and small amts. of the disulfones, and the 1,8-diethers yield more than 96% of the sulfonesulfonic acids and none of the disulfones; these SO_3H acids boiled with BuSH give the alkyl sulfone *Bu* thioethers.

Alkyl isopropyl anthraquinone 1,5-disulfones (m. ps.): *Me*, 235°; *Et*, 213°; *Pr*, 203°; *Bu*, 186°; *iso-Pr*, 222°; *iso-Am*, 172°. *Alkyl sulfone Bu thioethers* (m. ps. of the 1,5- and 1,8-derivs.): *Me*, 256°, 162°; *Et*, 210°, 140°; *Pr*, 204°, 132°; *Bu*, 162°, 126°; *iso-Am*, 189°, 121°. *Anthraquinone monothioethyleneglycol derivs.* (m. p. and color): 1-SCH₂-CH₂OH, 178°, orange; 1-SCH₂CH₂OAc, 146°, yellow; 1,5-(SCH₂CH₂OH)₂, 224°, orange; 1,5-(SCH₂CH₂OAc)₂, 199°, yellow; 1,8-(SCH₂CH₂OH)₂, 206°, red; 1,8-(SCH₂CH₂OAc)₂, 159°, yellow. *I*, from the BuS compd. with fuming HNO₃, seps. from cold H₂O with 3.59%, from hot H₂O with 2.05% H₂O. *1,5-Anthraquinone alkyl thioether Bu sulfones and alkyl Bu disulfones*, resp. (m. ps.): *Me*, 228°, 261°; *Et*, 214°, 194°; *Pr*, 201°, 220°; *Bu*, 162°, 184.5°; *iso-Am*, 152°, 203.5°; *Ph*, does not m. 350°, ----; *p*-nitrophenyl, above 300°. C. A. R.

Furfural- and difurfural- γ -methyleyclohexanones. MILLER, N. WOLFF. *Compt. rend.* 177, 197-9(1923).—Derivs. of monofurfural- α -methyleyclohexanones have been described (C. A. 16, 3312). W. now describes the prepn. of furfural- γ -methyleyclohexanone (I) and reduction products. γ - and β -Methyleyclohexanones contg. the group —CH₂COCH₂— should condense with OCH:CH:CH:CHO (II). γ -Methyleyclo-

hexanone and NH₂Na with II gave I, an oil which soon solidified, m. 43°. *Difurfural γ -methyleyclohexanone*, m. 94°, could not be prepd. by means of NaNH₂ but was prepd. by means of NaOMe.

Dipropargyl methylene ether. H. H. GUEST, *J. Am. Chem. Soc.* 45, 1804-7 (1923).—*Bis- α , β -dibromopropyl methylene ether*, obtained in 55% yield from BrCH₂-CHBrCH₂OH, HCl gas and paraformaldehyde after 6 days at room temp., b. 220°, also obtained in the same yield with FeCl₃ at 125-50° after 2 hrs., and in 20% yield with CaCl₂ as the catalyst. With a slight excess of powd. KOH in Et₂O suspension below 25°, it gives *bis- α -bromoalkyl methylene ether*, b. 135-40°, and with 4 mols. KOH in alc. after refluxing 2-3 hrs. 50% of *dipropargyl methylene ether* (I), b. 75-80°, b. 162°, whose *di-Ag* salt, granular ppt., turns brown 60°, explodes 110°, is insol. in NH₄OH and is very unreactive, being unchanged by BuBr in Et₂O even after 5 hrs.' boiling. It was hoped that by means of the Grignard reaction the higher homologs of propargyl alc. might be obtained from I, but although EtMgI reacts normally with I with steady evolution of C₂H₂, the product is resinous, insol. in Et₂O and C₆H₆ and has not been identified. C. A. R.

Shifting of acyl from nitrogen to oxygen in amino alcohols. MAX BERGMANN AND ERWIN BRAND. *Ber.* 56B, 1280-3(1923); cf. C. A. 15, 3277.—The technique for converting BzOCH₂CH(OH)CH₂NHBz (I) into BzOCH₂CH(OBz)CH₂NH₂ (II) has been simplified; the I is allowed to stand a short time with a moderate excess of POCl₃ or of SOCl₂ and treated with aq. HCl. On using SOCl₂ an intermediate product can be isolated; if 3 g. I in 3 parts SOCl₂ is kept 0.5-1.0 hr. at 18°, dry Et₂O ppts. 2.4 g. of the *HCl* salt, m. 130-1°, of *2-phenyl-5-benzoyloxymethylloxazoline*, BzOCH₂CH₂CH₂N(HCl).CPh.O (III), 0.3 g. of which, in 0.9 g. H₂O at 18°, gives in

a few hrs. 0.27 g. of II.HCl, m. 203°. Free III, m. 50-1°. *Acid sulfate*, m. 77-8°, dissolves instantly in a little H₂O and on rubbing seps. as the *neutral sulfate*, m. 152-3°. *Picrate*, m. about 205°, converted by short boiling with dil. alc. into the *picrate*, m. 192° (on rapid heating), of II. With POCl₃ instead of SOCl₂ the intermediate product, m. 102-3°, has apparently the compn. C₇H₉O₆NPCL₂; with C₆H₅N it gives III and with hot H₂O II.HCl. II is stable only in the form of its salts; in the free state, i. e., in a faintly alk. medium, it is converted back into I; in this reaction III is not an intermediate product. C. A. R.

Mercurated 1-methyl-1,2-dihydrobenzofurans. L. E. MILLS WITH ROGER ADAMS. *J. Am. Chem. Soc.* 45, 1842-54(1923); cf. C. A. 16, 3464.—The addn. of Hg⁺ salts to *o*-allylphenols is a general reaction, the yields being almost quant. in every case and the only difference being in the speed with which the reaction takes place. The 1-acetoxy- and 1-chloromercurimethyl-1,2-dihydrobenzofurans formed with Hg(OAc)₂ and HgCl₂ show the usual reactions of AcOHg and ClHg compds. with bromides and iodides, giving the corresponding BrHg and IHg compds. No Hg-bis or Hg-free compds. are formed with iodides. The halogen-Hg compds. react with the greatest ease with both alc. KCN and KSCN to form the NCHg and NCSHg compds. which it is impossible to convert into the Hg-bis compds. by longer refluxing. The HOHg compds. are readily obtained from the ClHg compds. with abs. alc. NaOH; they are readily neutralized by all types of org. and inorg. acids and ppt. insol. metallic hydroxides from neutral solns. of salts of the metals. The halogen-Hg compds. with alk. Na₂SnO₃ immediately ppt. metallic Hg and yield the corresponding allylphenol quant., with no indication of the

formation of an intermediate Hg compd.; with $(\text{NH}_4)_2\text{S}$, KSH or H_2S in dil. acid soln. they yield the allylphenol and HgS quant.; with cold satd. $\text{Na}_2\text{S}_2\text{O}_3$ is obtained the $\text{Na}_2\text{S}_2\text{O}_3\text{Hg}$ compd.; the only reagent that converts them into the bis-Hg compds. is Na-Hg; they are not affected by boiling MeI or AcCl ; with 2 atoms Br in CHCl_3 they ppt. a Hg^+ salt and yield 1-bromomethyl-1,2-dihydrobenzofuran. The reactions of these mercurated compds. offer still further convincing evidence that they are not "mol." substances but actually true addn. compds. *1-Acetoxymercurimethyl-1,2-dihydrobenzofuran derivs.* (m. p.): 6-Me, 113°; 5- and 4-Me and 4-Br, oils. *1-Chloromercurimethyl derivs.*: 6-Me, 91°; 5-Me, 127.5°; 4-Me, 99.5°; 4-Br, 108°; 6- CO_2H , 200° (decompn.); 6- CO_2Me , 107° (decompn.); 4- CO_2H , 212-3° (decompn.); 6-carboxyvinylene, 300° (decompn.). *1-Iodomercurimethyl derivs.*: 6-Me, 88°; 5-Me, 131.5°; 4-Me, 94°; 4-Br, 101°. *1-Bromomercurimethyl-4-bromo-1,2-dihydrobenzofuran*, m. 93°. *1-Hydroxymercurimethyl-1,2-dihydrobenzofuran*, m. 152°; 6-Me homolog, thick oil; 4-Me compd., m. 149°. *1-Tartratedi[mercurimethyl-1,2-dihydrobenzofuran]*, m. 192° (decompn.); 1-oxalate, m. 175°. *1-p-Nitrobenzoatemercurimethyl-1,2-dihydrobenzofuran*, m. 148° (6-Me homolog, m. 162.5°; 4-Me compd., m. 136.5°); 1-NCS compd., m. 112.5° (4-Me homolog, m. 102.5°); 1-NC compd., m. 162° (4-Me homolog, m. 148°); 1- $\text{Na}_2\text{S}_2\text{O}_3$ compd., glistening scales very sol. in hot H_2O , decomp. into HgS and o-allylphenol, darkens about 120°, decomp. more slowly at room temp., decomp. being complete in about 12 hrs. (4-Me homolog). *1,1-Mercuridimethylenebis-4-methyl-1,2-dihydrobenzofuran* (obtained in 35% yield with Na-Hg), m. 89.5°. Me 4-allyloxycinnamate (22.5 g. from 25.3 g. Me *p*-coumarate, 18 g. $\text{CH}_2=\text{CHCH}_2\text{Br}$ and 21 g. anhyd. K_2CO_3 refluxed in Me_2CO), m. 65.5°; 8.5 g. refluxed 2 hrs. at 230-45° rearranges into Me 3-allyl-4-hydroxycinnamate (7 g. crude product), 4 g. of which gently refluxed 4 hrs. with 10% NaOH gives 2.1 g. of the free acid, m. 169°. The conversion of ClHg into HOHg compds. by treatment in hot abs. alc. with NaOH is apparently a general reaction; MeHgOH was obtained in this way from MeHgCl .

C. A. R.

Syntheses of 3-hydroxy-5-thiotriazoles. E. FROMM and E. NEHRING. *Ber. 56B*, 1370-5 (1923); cf. Arndt, *C. A.* 16, 2509.—*1-Carbethoxy-4-phenylthiosemicarbazide* (I), from PhNHC(SNH)_2 boiled about 10 min. with ClCO_2Et in alc., m. 141°, does not condense with BzH ; refluxed 0.5 hr. with 1 mol. aq. NaOH, it yields 3-hydroxy-4-phenyl-5-thiotriazole (II), PhN.C(OH):N.N:CSH , prisms with 1 H_2O , sinters 130-40°.

m. 193°, loses its H_2O at 130° and takes it up again on recrystn., even from 96% alc., gives with PhCH_2Cl and alkali in boiling alc. the 5-thiobenzyl deriv. (III), m. 158°, also obtained from I with 1 equiv. each of alkali and PhCH_2Cl and from the Pb salt of II with boiling PhCH_2Cl . 2-Bz deriv. of III, m. 122°. Me deriv., from III with Me_2SO_4 and NaOH, m. 126°. PhNHNH , salt of II, m. 169°. Disulfide of II, from II in alc. with Br water, m. 286°, decompd. by boiling NaOH, with formation chiefly of the Na salt of II but also with distinct formation of SO_2 . ClCO_2Et and $\text{NH}_4\text{CSNHNH}_2$ in C_2H_5 usually form mixts. which cannot be sepd. but in 1 case was isolated a S-free substance, m. 130°, having the compn., $\text{C}_7\text{H}_{13}\text{O}_3\text{N}_4$, of dicarbethoxysemicarbazide. *1-Carbethoxythiosemicarbazide* (IV), from $\text{NH}_2\text{CSNHNH}_2$ and 1 equiv. ClCO_2Et boiled 1 hr. in about 10 parts abs. alc., m. 184°, stable towards acids, does not condense with BzH , but is altered by boiling alkali. $\text{PhCH}_2\text{SC(NH)NHNHCO}_2\text{Et}$ (V), from IV, PhCH_2Cl and NaOH in boiling alc., m. 145°. IV boiled with 2 equivs. aq. NaOH splits off EtOH and with AcOH and Pb(OAc)_2 yields the Pb salt of 3-hydroxy-5-thiotriazole (VI), m. 202°. 5-Thiobenzyl deriv. (VII), from IV boiled with PhCH_2Cl and 2 equivs. aq. alkali, from the above Pb salt with PhCH_2Cl in alc., or from V boiled with 1 equiv. alkali, m. 182°. PhNHNH , salt of VI, faintly yellow, m. 155°. Di-Ac deriv. of VII, m. 89°. Disulfide of VI, m. 245°, has no H_2O of crystn., contrary to Arndt's product.

C. A. R.

Thioflavonones, thiochromanones and -chromonols. F. ARNDT, with W. FLEMMING, E. SCHOLZ and V. LÖWENSOHN. *Ber. 56B*, 1269-79 (1923).—The present results are published earlier than had been intended because of the appearance of the papers of Krollpfeiffer and Schäfer (*C. A.* 17, 2422) and of Zahn (*C. A.* 17, 2425). The purpose of the work was to det. whether in the flavone dyes the replacement of the ring O by S would produce a deepening in color similar to that of thioindigo as compared with oxindigo and whether from 6-membered, similarly constituted 5-contg. ring systems thioindigoid dyes could be obtained. β -*p*-Tolylmercaptohydrocinnamic acid (I), m. 106°, is obtained in 63% yield (really quant., as the $\text{MeC}_6\text{H}_4\text{SH}$ and $\text{PhCH:CHCO}_2\text{H}$ which do not react are recovered) from 15 g. $\text{PhCH:CHCO}_2\text{H}$, 12 g. *p*- $\text{MeC}_6\text{H}_4\text{SH}$, 40 g. AcOH satd. with HCl and 10 g. AcOH satd. with HBr heated 5 hrs. at 100° in a sealed tube. β -Phenylmercaptohydrocinnamic acid (II), obtained in 75% yield, m.

85-6°. Refluxed 15-20 min. on the H₂O bath with 60 g. POCl₃ 13 g. **I** yields, together with 3 g. unchanged **I**, 8.2 g. 6-methylthioflavanone, MeC₆H₄COCH₂CHPh.S (III),

m. 96°, insol. in alkalis, easily sol. in concd. H₂SO₄ with crimson color. If 12 g. finely powdered **I** and 2 vols. P₂O₅ are heated 4 hrs. at 100° in a closed vessel, EtO exts. from the resulting brownish mass about 3.5 g. **III** and from the residue can be isolated 6-methylthioflavone, m. 149-50° (Ruhemann, C. A. 8, 348, gives 153°). Thioflavanone, m. 55-6°, dissolves in H₂SO₄ with bright red color. 3-Benzal deriv. of **III**, m. 108-9°, from **III** in a slight excess of warm BzH treated 10 min. with HCl gas and allowed to stand in a closed vessel overnight, is identical with the product obtained from 3,4-Ac(MeS)C₆H₃Me (C. A. 3, 2577); phenylhydrazon, m. 206°, sol. in H₂SO₄ with orange-red color. 3-Benzalthioflavanone, pale yellow, m. 132-3°, sol. in concd. H₂SO₄ with dark brown-red color but without the given dichroism of its Me homolog. All attempts to convert these thioflavanones into thioflavonoids failed. AnNO₂ and HCl and other nitrosating agents give under gentle conditions usually no alkali sol. products while under more energetic treatment H₂O₂ is oxidized away with formation of 5-methylthionaphthenequinone, bright red, m. 145-6°, previously described (Ger. pat. 212,782, C. A. 3, 2874) as being brown and m. 113-4°. On the other hand, **III** smoothly condenses in boiling alc. contg. a few drops of concd. KOH with p-ONC₆H₄-NMe₂, giving 80% of 6-methylthioflavonol p-dimethylaminoanil, brown red, m. 166-7°, sol. in AcOH with green, in H₂SO₄ with pale red color, not decomd. by boiling 65°. H₂SO₄ even after several hrs. 6-Methylthioflavonol anil, obtained in 70% yield from PhNO, yellow, m. 172-3°; in an earlier expt. with impure PhNO (crude product of the oxidation of PhNH₂OH with K₂Cr₂O₇) was obtained a stereoisomer, m. 91-2°, whose m. p. did not change on recrystn. until it was seeded with the higher melting form, when it changed over into the latter; both forms dissolve in H₂SO₄ with brown red color changing on boiling to dirty brown; after boiling several hrs. and cooling, **III** seps. a p-Tolylmercaptopropionic acid (IV), obtained almost quant. from p-MeC₆H₄SH in NaOH slowly treated with aq. ClCH₂CH₂CO₂H and brought to a boil, m. 70°, sol. in H₂SO₄ with red color (owing to the formation of the thiochromanone). β-Phenyldimercaptopropionic acid, prepd. from PhSH, m. 58°. IV, gently warmed with concd. H₂SO₄ until it dissolves and heated a few min. longer at 60°, almost quant. yields 6-methylthiochromanone (V), m. 41°, volatile with steam, sol. in H₂SO₄ with red color. Thiochromanone, m. 28°, sol. in H₂SO₄ with red color. Benzal deriv. of V, yellow, m. 119.5°, sol. in H₂SO₄ with intense dark brown color (dark green in thin layers). 6-Methylthiochromonol p-dimethylaminoanil, brown-red, m. 193°, sol. in aq. mineral acids with yellow color. Thiochromonol p-dimethylaminoanil, m. 142°. 6-Methylthiochromonol, from the anil boiled 5-10 min. in a little 50-60% H₂SO₄, faintly yellow, m. 167-8°, difficultly sol. in concd. H₂SO₄ with yellow color, forms intensely yellow, difficultly sol. Na and K salts. Thiochromonol, yellowish, m. 172°. C. A. R.

Stereochemistry of tervalent nitrogen. Action of propylmagnesium bromide on quinoline methiodide. JAKOB MEISENHEIMER AND MAX SCHÜTZE. Ber. 56B, 1533-62 (1923).—Years of study of the problem have convinced M. that a satd. tervalent N atom can give rise, as a center of asymmetry, to stereoisomers in only very special cases, if at all. Freund and Kessler (C. A. 13, 2660) describe several pairs of stereoisomeric 1-methyl-2-alkyltetrahydroquinolines, the existence of which they ascribe to the presence of 2 asym. atoms, a C and a N atom. A repetition of their work, however, has shown that it is entirely wrong. From PrMgBr and quinoline-MeI is obtained 1-methyl-2-propyl-1,2-dihydroquinoline (I), which can be obtained pure by distn. *in vacuo* (v. Braun and Aust, C. A. 9, 321). F. and K., however, distd. their crude product under atm. pressure and overlooked the fact that at such a high temp. (270°) **I** decomps. to a considerable extent into CH₄ and 2-propylquinoline (II), a smaller amt. is reduced to 1-methyl-2-propyl-1,2,3,4-tetrahydroquinoline (III) and the rest distils undecompd. or changes into products whose nature has not yet been detd. If this decompn. is completed by long boiling under reflux, there are obtained about 40% **II** and 10% **III**. F. and K.'s supposedly pure **I** was therefore such a mixt., which explains all their surprising observations. With MeI are formed the cryst. methiodides of **II** and **III**, a mixt. of which has about the same properties as F. and K.'s "I-MeI." Likewise, reduction of their product gives a mixt., not of 2 stereoisomers, but of 2-propyltetrahydroquinoline (IV) and **III**. There can therefore be no doubt that **III** does not exist in 2 stereoisomeric forms; this is also most probably true of the analogous 2-iso-Bu compd. and the similar cases of isomerism of dihydrocarnitine and dihydrodrastine described by F. **I**, obtained in 60-70% yield with a 1/2 mol. excess of PrMgBr if a carefully dehydrated quinoline-MeI is used, b₁₀ 152°; picrate, orange, m. 72°, cannot be

recrystd. unchanged from any solvent. II, b_p 130-1°, faintly yellow-green, sol. in HCl without color; *picrate*, light yellow, m. 163-4°; *methiodide*, light yellow, m. 180°, decomps. completely on repeated crystn. IV (8.5 g. from 10 g. II in 20% HCl on the H₂O bath with Sn), b_p 140-0.5°, stable oil with violet fluorescence; HCl salt, m. 221-2°; Bz deriv., m. 102°; *methiodide*, light yellow, semi-solid mass; *picrate*, gradually solidifying brown oil with 1 mol. solvent from H₂O, m. 56-60°, light yellow needles with 0.5 mol. solvent from PhMe, m. 70-115°, red-brown to orange solvent-free plates from alcs. and Et₂O, m. 125° (v. B. and A. give 143°). III (9 g. from 10 g. I with Na in alc.), faintly yellow, b_p 144.5°; *picrate*, m. 123°; *methiodide*, m. 180-200° (foaming), depending on the rate of heating. The *picrate* of I (12 g.) dissolved in 400 cc. boiling alc. deposits on cooling brown crystals from which, by tedious fractional crystn., can be isolated 4 g. of the light yellow 1-methyl-2-propylquinolinium *picrate* (identical with a product obtained from II.MeI and *picric acid* in alc.), and 4 g. of a deep red-brown dark gleaming compd., C₁₃H₁₇N.C₆H₅O₇N, m. 122°, which is probably an *indole picrate*, C₈H₄.CH:CH.NMe(C₆H₅)OC₆H₅(NO₂)₃; both *picrates* are completely decompd. by hot

NaOH into amorphous products.

C. A. R.

bs-Tetrahydroquinolines and their derivatives. II. JULIUS V. BRAUN, WALTER GMELIN AND ADAM SCHULTHEISS. *Ber.* 56B, 1338-47(1923); cf. C. A. 17, 1965.—Below are given the relative % of *bs*- and *py*-tetrahydro derivs., resp., obtained in the catalytic hydrogenation of methylated quinolines: 8-Me, 0, 100; 7-Me, 0, 100; 6-Me, 0, 100; 5-Me, not studied; 4-Me, 33, 66; 3-Me, 33, 66; 2-Me, 4, 96; 2,3-Me₂, 44, 56; 2,4-Me₂, 80, 20; 2,3,4-Me₃, > 80, —. These results, in connection with those reported in the earlier paper, show that substitution in the C₆H₄ nucleus prevents hydrogenation of that nucleus while loading of the C₆H₃N nucleus with substituents favors hydrogenation of the C₆H₅ nucleus. Thus, by suitable substitution of the quinoline it is possible to obtain any desired relative hydrogenation of the 2 nuclei, and as the *bs*-tetrahydro compds. are smoothly reduced in the C₆H₃N nucleus by Na and alc. the way is now open for the prepn. of an extensive series of decahydroquinolines. To the reduced Ni salt in tetra- or decahydronaphthalene suspension in the pressure hydrogenation app. described in earlier papers was added the methylated quinoline, in the same solvent, and the temp. was raised until the absorption of H began (110-90°); when the reaction was ended, the mixt. was dild. with Et₂O, filtered from the Ni, shaken out with acid, the ext. made alk. and the tertiary *bs*-tetrahydro bases were sepd. from the isomeric secondary *py*-compds. by treatment with BzCl. *py*-8-Methyltetrahydroquinoline; N-NO deriv., m. 51°; Bz deriv., m. 108°. 7-Me isomer, b_p 130-2°; Bz deriv., m. 70-2°; *picrate*, m. 173-4°; HCl salt, m. 175°. *py*-Tetrahydrolepidine, b_p 130°; Bz deriv., m. 129°. *bs*-Isomer (4-methyl-5,6-tetramethylene-pyridine), b_p 122°, does not react with HNO₃; HCl salt, m. 203-4°; *picrate*, m. 170°; *methiodide*, darkens 179°, m. 183°. With 3 times the calcd. amt. of Na in alc. the base gives the *decahydro compd.*, b_p 105°; HCl salt, m. 205°; *picrate*, m. 159°; *phenylthiourea*, m. 105°; with MeI and alkali the *decahydro base* gives a compd. C₁₂H₁₂N₂, m. 235°. *py*-Tetrahydro-3-methylquinoline, b_p 116-8°; Bz deriv., m. 84°; HCl salt, m. 207°; *picrate*, m. 155°; NO deriv., oil. *bs*-Isomer, b_p 126-7°; HCl salt, oil; *chloroplatinate*, decomps. 219°; *picrate*, m. 171°; *methiodide*, m. 162°. *Decahydro compd.*, b_p 125-7°, m. 70-1°; NO and Bz derivs., oils; *picrate*, m. 75°; HCl salt, sinters about 210°, m. 218°. *bs*-Tetrahydroquinadine, b_p 101-4°, d_4^{25} 1.0000; *picrate*, lemon-yellow, m. 154°; HCl salt, slightly hygroscopic, m. 164°; *methiodide*, quite hygroscopic, m. 118°. *py*-Isomer, b_p 115-6°; Bz deriv., m. 116°; HCl salt, m. 128-30°. The 2,3-dimethylquinoline (I), m. 68-9°, was prepd. by Pfitzinger's method by decarboxylation of the 2,3-dimethylcinchoninic acid (II) obtained from isatin and MeCOEt (*J. prakt. Chem.* 56, 314(1897)); it crysts. slowly and incompletely from the oily crude product and is freed from the accompanying oil by pressing on clay. To det. whether the I thus obtained is really pure, the crude II was converted into the Ag salt and heated several hrs. on the H₂O bath with an excess of MeI; the resulting Me ester, warmed a short time at 40° on clay, can be sepd. into a fraction, m. 120-1°, hydrolyzed by aq. alc. KOH to the pure II, the latter on decarboxylation yielding I, while the part of the ester which goes into the clay and is extd. with Et₂O b_p 176-8°, m. 38°, and is hydrolyzed to 2-ethylcinchoninic acid. As the I obtained from the ester mixt. agrees completely in its properties with that isolated from the base mixt. it can with all probability be assumed to be homogeneous. *py*-Tetrahydro-2,3-dimethylquinoline, b_p 127-8°, d_4^{25} 1.0048; Bz deriv., m. 94-5°; HCl salt, m. 154°; *picrate*, m. 161°; NO deriv., yellow, m. 56°. *bs*-Isomer, b_p 125-6°, m. 38°; HCl salt, very hygroscopic, m. 192°; *picrate*, m. 169°; *methiodide*, m. 117°. *Decahydro compd.*, b_p 95-7°, d_4^{25}

0.9152; *picrate* and *NO deriv.*, oils; *HCl salt*, does not m. 280°; *methiodide*, m. 199°. *py-Tetrahydro-2,4-dimethylquinoline*, b_{12} 125-7°; *Bz deriv.*, m. 110°. *bz-Isomer*, b_{12} 122-3°; *picrate*, m. 141-5°; *HCl salt*; *NO deriv.*, yellow oil; *quaternary methiodide*, sinters about 200°, m. 210°. III. Tricyclic compounds. JULIUS V. BRAUN, ADOLF PERZOLD AND ADAM SCHULTHEISS. *Ibid* 1347-50. —As expected, when the $C_{11}H_8N$ nucleus of quinoline is substituted with $-CH_2CH_2-$ and $-CH_2CH_2CH_2-$ (instead of 2 and 3 Me groups), catalytic hydrogenation results in the formation of considerable amts. of the *bz-tetrahydro* derivs. (49 and 48%, resp.) and these can, in turn, be easily further reduced to the perhydrogenated tricyclic bases. *asym-Octahydroacridine*, b_{12} 183°, m. 84°; *Bz deriv.*, m. 104°. *sym-Isomer*, b_{12} 175°, m. 69°, reacts with neither acid chlorides nor HNO_3 ; *HCl salt*, oil; *chloroplatinate*, m. 199-200°; *picrate*, m. 195°; *methiodide*, m. 159°. *Perhydroacridine*, $C_{15}H_{12}N$, m. 80°; *HCl salt*, does not m. 300°; *picrate*, m. 167°; *NO deriv.*, faintly yellow, m. 217°; *quaternary methiodide*, m. 206°. *py-Tetrahydro- α,β -trimethylenequinoline*, b_{12} 169-71°; *Bz deriv.*, m. 157°; *HCl salt*, m. 113°; *picrate*, m. 154°; *NO deriv.*, m. 154°. *bz-Isomer* (2,3-trimethylene-5,6-tetramethylene-pyridine), b_{12} 160-1°, slowly becomes yellowish in the light; *HCl salt*, m. 91°; *picrate*, yellow, m. 160°. *Perhydroamine*, $C_{10}H_{12}N$, b_{12} 140-2°; *picrate*, yellow, m. 171°; *HCl salt*, decomp. 255-8°; *NO deriv.*, yellow oil. C. A. R.

5-Methyl-*py-tetrahydroquinoline* and its fission. JULIUS V. BRAUN AND THEO KÜHNLEIN. *Ber.* 56B, 1351-2(1923).—5-Methyl-*py-tetrahydroquinoline*, b_{12} 130-1°, is obtained almost quant. from 5-methyl-8-chloroquinoline in 50 parts abs. alc. with 5 parts Na; *HCl salt*, m. 228°; *picrate*, m. 156°; *NO deriv.*, m. 66-7°; *Bz deriv.*, m. 121°. The *Bz deriv.* heated with 1 mol. PCl_5 until a homogeneous melt resulted and then raised in the course of 0.5 hr. to 140° gave 35% *N-benzoyl-3-methyl-2- γ -chloropropyl-aniline* (*vic-methylchloropropylbenzanilide*), m. 102-3°. C. A. R.

Phenanthrene series. XXXIV. Obtainment of 2-hydroxymorpholquinone (2,3,4-trihydroxyphenanthrenequinone) from 4-nitrophenanthrenequinone. JULIUS SCHMIDT AND OTTO SCHAIRER. *Ber.* 56B, 1331-7(1923); cf. C. A. 16, 3650. —The only degradation product of the opium alkaloids hitherto prepd. starting from phenanthrene is morpholquinone (I), made by a process which is very tedious, as the prepn. of the starting material, 3-nitrophenanthrenequinone, from phenanthrenequinone (II) is unsatisfactory, and the final yield of I is quite poor. Attempts were therefore made to obtain I or one of its substitution products from 4-nitrophenanthrenequinone and as the yield of this by the method previously described (heating II with HNO_3) is only 20-5%, S. and S. tried to work out a better method; they hoped, by the introduction of orienting influences, to direct the NO_2 group exclusively to the 4-position in II. They accordingly studied the action of HNO_3 on the acetates of phenanthrenedihydroquinol (III), but neither of them gave III. 4-Hydroxyphenanthrenequinone (IV), however, with HNO_3 quite smoothly gives the 2,3-di- NO_2 deriv. (V), and this through the di- NH_2 and bisdiaz compds. yields 2,3,4-trihydroxyphenanthrenequinone (VI), but here again the diazotization proceeds so unsatisfactorily that the final yield of VI is small. Monoacetate of III, from the freshly prepd., still moist III heated a short time with about 2 parts Ac_2O , sinters 178°, m. 181-2°, dissolves instantly in cold NaOH, the soln. soon becoming yellow-brown and finally depositing a green ppt. which redissolves on heating; the soln. is now colorless and probably contains diphenyleneglycolic acid. Short boiling with fuming HCl converts the acetate into $AcOH$ and III. Diacetate, from the monoacetate refluxed 1 hr. with 3-4 parts Ac_2O , m. 202°; 5 g. suspended in 50 cc. $AcOH$ and 50 cc. Ac_2O and slowly treated at -5° with 40 cc. Ac_2O and 40 cc. HNO_3 (d. 1.45) and allowed to stand 12 hrs. gives 2,7-dinitro-9,10-diacetoxypheanthrene, yellow, m. about 280° (decompn.), converted by long boiling with dil. HNO_3 contg. some $AcOH$ into 2,7-dinitrophenanthrenequinone. V, obtained in about 50% yield from IV in 1 g. portions heated 3-4 min. over a free flame with 10 cc. HNO_3 (d. 1.35) and at once poured into a little cold H_2O and purified by repptn. from $NaHCO_3$ with HCl, bright red, m. 248° (decompn.), sol. in $NaHCO_3$ with dark green color, easily converted by alkalis into the corresponding diphenyleneglycolic acid, only slightly sol. in concd. H_2SO_4 with pink color; *acetate*, red-brown, m. 233° (decompn.); *mono-oxime*, orange, deflagrates 214-5°. 2-Hydroxy-2,3-dinitrophenanthrophenazine, from V in alc. suspension boiled 2 hrs. with concd. aq. $\nu-C_6H_4(NH_2)HCl$, light brownish, m. 240° (decompn.). With $K_2Cr_2O_7-H_2SO_4$ V gives phthalic acid. 4-Hydroxy-2,3-diaminophenanthrenequinone, from V in fuming HCl with granulated Sn, followed by evapn. to dryness of the soln. of the hydroquinol HCl salt, gleaming black powder; diazotized in cold fuming HCl, filtered from the by-products and boiled, it gives a small amt. of VI, brown-red powder, m. 185° (decompn.); VI is a good mordant dye, dyeing cotton on a Cr mordant in aq. suspension violet, on Fe brown and on Al pink. 2,3,4-Trihydroxyphenanthrophenazine, brown, m. about 255° (decompn.). C. A. R.

Seven-membered rings containing sulfur and nitrogen. FRITZ MAYER AND CARL HORST. *Ber.* 56B, 1415-23(1923).—From 30.6 g. (*o*-O₂NC₆H₄)₂S₂ in 100 cc. alc. at 60° slowly treated with a concd. soln. of 14 g. crystd. Na₂S and 8 g. NaOH, dild. with 500 cc. hot H₂O, quickly cooled, filtered and heated 15 min. with 25 g. ClCH₂CH₂CO₂H (just neutralized with Na₂CO₃) in 100 cc. H₂O is obtained 33 g. 2-nitrophenylthiohydricrylic acid, m. 145°; *Me ester*, light yellow, m. 76°; *Et ester*, green-yellow, m. 69°. With NH₄OH-FeSO₄ the acid gives 77% of the *NH₂ acid* (I), m. 84°; *HCl salt*, m. 180°; *Et ester HCl salt*, m. 144°, dissociates in H₂O with deposition of the free ester as an oil. *z*-HO acid (0.1 g. from 5 g. of I diazotized in H₂SO₄ and allowed to stand 48 hrs.), faintly yellow, m. 86-8°. I raised to 190° in the course of 45 min. and kept at this temp. until the elimination of H₂O is complete gives almost quant. *benzoketohydrohepta-1,5-thiazine*, C₈H₄S.CH₂.CH₂.CO.NH (II), m. 215-6°, also obtained from I.HCl at

190-200° and by distn. of the *Me ester* of I; it dissolves in both dil. and concd. NaOH but with immediate evolution of a mercaptan-like odor; heated 4 hrs. at 110° in a sealed tube with concd. HCl, it gives I.HCl. *z*-Cyanophenylthiohydricrylic acid (3 g. from 8.6 g. I by the Sandmeyer method), m. 92-3°; I g. heated 7 hrs. at 110° with concd. HCl gives the *z*-carboxylic acid, m. 190°, also obtained in 0.5 g. yield by treating in a little dil. NaOH with H₂O₂ the *keto acid* *o*-HO₂CCOC₆H₄SC₆H₄CO₂H, yellow, m. 138° (*oxime*, m. 92°), which results in 2.3 g. yield from 2.96 g. thionaphthenequinone in Na₂CO₃; boiled 0.5 hr. with ClCH₂CH₂CO₂Na. *z*(*?*)-Chlorobenzoketohydrohepta-thiazine (2.5 g. from 3 g. II in boiling C₆H₆ slowly treated with 1.2 g. SO₂Cl₂), faintly yellow, decomp. 138-43°, turns brown on heating, gives a yellow oil with dil. NaOH; 2 g. boiled 0.5 hr. in alc. gives 2 g. of the *z*(*?*)-EtO deriv., m. 172-3°; *MeO compd.*, m. 175-6°; *z*(*?*)-thioglycolic acid deriv., m. 209-10°; *z*(*?*)-Di-Cl compd., from II and the necessary amt. of SO₂Cl₂ boiled 15 min. in PhCl, m. 254-5°, is not changed by long heating with alc; *Na salt*, decomp. 135°. I or II with boiling Ac₂O yields a compd., m. 87°, which is apparently the Ac deriv. of I (found, C 52.1, H 5.5, N 6.04, S 13.5%). *z*-Nitrophenylsulfopropionic acid (4 g. from 5 g. of the thiohydricrylic acid in Na₂CO₃ and KMnO₄ in the H₂O bath), m. 144°; *Et ester*, m. 45°. The acid is also obtained with H₂O₂ in AcOH; 2.6 g. with NH₄OH-FeSO₄ gives 1.5 g. of the *NH₂ acid*, m. 105° (*HCl salt*, m. 181-6°), 5 g. of which, heated up to 210°, yields *benzoketohydrohepta-1,5-sulfazone*, C₈H₄SO₂.CH₂.CH₂.CO.NH, m. 246-7°, obtained in

better yield (3 g.) from 5 g. II in AcOH with H₂O₂ below 70°; with concd. HCl at 125° it gives I.HCl. *z*-Nitro-4-chlorophenylthiohydricrylic acid (yield, 64%), light yellow, m. 158-9°; *Et ester*, light yellow, m. 77°. *NH₂ acid*, m. 90°; *HCl salt*, m. 162-3°. *γ*-Chlorobenzoketohydroheptathiazine (III), obtained almost quant. from the *NH₂ acid* heated up to 165° in the course of 2 hrs., m. 217°; both it and the *NH₂ acid* with Ac₂O yield a compd., m. 112-3°, which is apparently the Ac deriv. of the acid. *z*(*?*)-Di-Cl deriv. of III, from III in boiling C₆H₆-PhCl with SO₂Cl₂, decomp. 207°; *z*(*?*)-EtO compd., m. 180°. *z*-Nitro-4-chlorophenylsulfopropionic acid, m. 183-4°. *γ*-Chlorobenzoketohydroheptasulfazone, m. 269°. C. A. R.

Sulfamide (TRAUBE, REURKE) 6. Compounds of AlBr₃ with P bromides and organic bromides (PLOTNIKOV) 6. Structure of complex compounds (PLOTNIKOV) 6. The electronic theory of valency. II. Intramolecular ionization in organic compounds (LOWRY) 2. Structure association (HELLER) 2. The mesomorphic states of matter (FRIEDEL) 2.

BIGELOW, LUCIUS A. AND BOYES, KURWIN R.: **Organic Chemical Transformations.** New York: D. Van Nostrand Co. 4 pp. 20 cents.

REMSEN, IRA: **Organic Chemistry.** Revised and enlarged by W. R. Orndorff. New York and London: Macmillan & Co., Ltd. 567 pp. Reviewed in *Chem. Age* (London) 9, 87(1923) also in *Chem. News* 127, 79(1923).

Chlorinating organic compounds. A. BOAKE, ROBERTS, & Co., LTD., and O. SILBERRAD. *Brit.* 193,200, Dec. 16, 1921. The chlorination of org. compds. is carried out by means of SO₂Cl₂ in conjunction with AlCl₃ and S₂Cl₂. The last reagent may be omitted if substances, such as S and CS₂, capable of yielding S₂Cl₂ under the conditions of reaction, are present. An example describes the chlorination of *p*-dichlorobenzene to yield tetrachlorobenzene with lesser amts. of tri-, penta- and hexachlorobenzene. The chlorination of anthraquinone, indanthrene, and naphthalene and its derivs. is also referred to.

Formaldehyde. T. A. F. HOLMGREN. Swed. 53,822, Feb. 21, 1923. Water gas is brought into contact with metals or metal compds.

Separating methanol from sulfite alcohol. AKTIEBOLAGET ETHYL. Swed. 53,318, Mar. 7, 1923. The mixt. is distd. in a column app. Suitable quantities of EtOH are taken out at the bottom of the app. where the temp. corresponds to the b. p. of the dis. charged alc.

Pyrocatechol, phenols and acids from residues from destructive distillations. K. H. A. MELANDER and I. H. WALLIN. Swed. 51,200, Apr. 4, 1923. Evapd. cellulose waste liquor is neutralized with alkali or lime and subjected to destructive distn. at 300–500° under application of superheated steam. The distn. residues are decompd. by mineral acids into free phenols and org. acids which are sepd. in the usual ways.

Catalyst for the production of acetone from acetic acid. AKTIEBOLAGET STOCKHOLMS SUPERFOSFATFABRIKKER. Swed. 53,894, Feb. 28, 1923. Smelted Al is granulated to a porous structure and placed in a soln. or suspension of catalyzing substances, which is evapd. to dryness.

Urea from cyanamide. AKTIEBOLAGET WARGOENS and J. H. LIDHOLM. Swed. 54,246, Apr. 11, 1923. A 10% soln. (or more) of cyanamide is treated with mineral acids in amts. of not more than 20% of the cyanamide (by wt.).

Condensation products of formaldehyde and urea, etc. F. POLLAK. Brit. 193,420, Feb. 17, 1923. Before heating the sol. initial condensation compds. of HCHO and urea, thiourea or their derivs. to transform them into insol. products, a substance is added which is capable of fixing or decompg. the excess of HCHO present. Such substances are urea, thiourea or their derivs., phenols or their derivs., and H₂O₂. Dimethylolurea may replace the initial condensation compd. The HCHO may be used in soln., in the gaseous state, or in the form of its polymers. According to the examples, (1) urea is condensed with com. HCHO in the presence of a little (CH₃)₂N₂ to form the sol. initial condensation compd.; urea is then added, with or without some AcONa, and after further heating, the product is poured into a mold and hardened at temps. of 60–100°; (2) dimethylolurea is dissolved in boiling H₂O, urea then added and the product treated as before. Cf. 151,016 and 171,094 and C. A. 16, 995.

11—BIOLOGICAL CHEMISTRY

PAUL E. HOWE

A—GENERAL

FRANK P. UNDERHILL

Is cystine synthesized in the animal body? J. A. MULLOON, G. J. SHIPLE and C. P. SHERWIN. *Proc. Soc. Exptl. Biol. Med.* 20, 467 (1922). Bromobenzene is detoxicated in dogs by joining cystine; the amino group of the latter is then acetylated. Dogs were given a carbohydrate diet and fed bromo benzene each day; S was added by giving successively for 2-day periods Na₂SO₄, taurine, CaSO₄, Na thiocyanate and ethylaminomercaptan; no detoxication by cystine resulted. The addn. of N in the form of AcONH₄ or gelatin also gave negative results. C. V. B.

The nature of the antitryptic action of serum and its biologic significance. A. A. EPSTEIN. *Proc. Soc. Exptl. Biol. Med.* 20, 48–50 (1922).—The inhibition of tryptic digestion by serum is due slightly to globulin and largely and proportionately to the amt. of albumin present. Trypsin was quant. recovered, after prolonged incubation with serum, by pptg. the proteins with colloidal Fe or EtOH. After digesting casein, no trypsin was recovered. Trypsin was recovered from a mixt. of serum, trypsin and casein when digestion did not take place. The action is in the nature of an interference phenomenon. C. V. B.

The decomposition of cellulose in nature. C. NEUBERG. *Naturwissenschaften* 11, 657–9 (1923).—Chiefly a review and discussion. It is now almost certain that AcH is always formed during the decompn. of carbohydrates by organisms as already proved in sp. cases by the extensive work of N. New investigations now indicate that AcH is also an intermediate product of the H and CH₄ fermentation of cellulose. C. C. DAVIS

The hydrogen-ion concentration of soils and natural waters in relation to animal distribution. W. R. G. ATKINS. *Rept. Brit. Assoc. Advancement Sci.* 1922, 373.—A close connection exists between the distribution of plants and the soil reaction, and furthermore many animals (especially insects) are related to sp. plants. These facts

are correlated, with the aid of several sp. examples (earthworms, snails, mosquito larvae, etc.), to show that a direct relation exists between the *distribution of certain animal life and the soil reaction*.

C. C. DAVIS

The absorption of ultra-violet rays by living tissue, spectacle glass, and some physiological solutions. L. J. C. MITCHELL. *Med. J. Aust.* 1922, ii, 268-71; *Physiol. Abstracts* 8, 72.—Working with Hilger's quartz spectrograph, M. gives data as to the power of various kinds of glass and salt solns. to absorb ultra-violet light. The cornea proved to be the best filter of ultra-violet light among all the transparent media of the eye, except the lens.

H. G.

New experimental studies on the physiology of smell. A. M. CALDERIN. *Siglo méd.* 69, 365-7, 395-7(1922); *Physiol. Abstracts* 8, 54.—(1) The strength of the olfactory sensation for any substance depends principally upon the degree of its soly. in the watery layer which surrounds the olfactory cells, and in the lipoids of the membrane and protoplasm of these cells. (2) The relation of soly. to strength of olfactory sensation is designated as the "olfactory capacity" of a substance, and can only be applied to substances which belong to the same chem. series and their isomers. The soly. in lipoids is of particular consequence in raising the value of the olfactory capacity.

H. G.

Balancement of ions. T. P. FEENSTRA (Utrecht 1922); *Physiol. Abstracts* 8, 99; cf. *C. A.* 17, 2001.—The balancement of salts in physiol. solns. is the attainment of a mutual equil. in the ion action. Anions are of small importance in this process; it is independent of temp.; the two last-named facts already find expression theoretically in the formula of Nernst. The breadth of variation in the different cases makes it advisable to speak of a zone of balancement. The electrolytical tension of the solns. was calcd. from Hofmeister's data; the equil. between the ions in different physiol. solns. from Nernst's formula was extended for that purpose. The calcs. of the relative balancements in physiol. solns. for warm-blooded animals which were made from this formula (at the isoelec. point, the concn. of the electrolyte has the same value as the const. of the tension of the electrolytical soln.) proved to correspond closely with the exptl. data. For cold-blooded animals the differences between calcs. and expts. are greater, probably through the fact that Hofmeister's calcs. were made for proteins of warm-blooded animals. Conclusions: Balancement is a phenomenon of a general sort in the sphere of ion action; radio-physiol. antagonism, on the contrary, is a sp. action of radioactive substances in a physiol. soln. For cells whose normal function depends on the presence of ions one must take into consideration (a) whether the ions in the surrounding fluid are balanced or not, (b) the sp. nature of the ions in such a fluid.

H. G.

Protein reactions. R. F. HUNTER. *Chem. News* 127, 134-5(1923).—The behavior of egg albumin toward a large variety of reagents is described. No definite conclusions are drawn.

E. H.

The relative concentration ratios of some constituents of the urine. The relative concentration ratios of urea, creatinine, inorganic phosphate and uric acid. S. W. F. UNDERHILL. *Brit. J. Exptl. Pathol.* 4, 117-26(1923); cf. *C. A.* 17, 2735.—In the cat the kidneys may concentrate urea, creatinine and inorg. phosphate to varying and unequal extents. The excretion rates of urea, creatinine and inorg. phosphate show a general relationship, rising and falling together though not to the same relative degrees. The correlating factor is probably the blood flow through the kidney. After injection, urea and creatinine leave the blood stream extremely rapidly while the rate of disappearance of inorg. phosphate is not quite so rapid, and a greater proportion remains in the blood as compared with that passing into the tissues. It is considered that the results of the expts. on the relative concn. ratio of urea, creatinine and inorg. phosphates are incompatible with the "filtration reabsorption" hypothesis of kidney function in its present form. It is concluded that the kidneys must actively secrete one or more of these substances into the urine.

HARRIET F. HOLMES

Arginase. VII. Arginase in the enteric mucus and in the enteric secretion. ANTONINO CLEMENTI. *Atti accad. Lincei* [v] 31, ii, 559-61(1922).—By the method previously described (*C. A.* 17, 3198) C. demonstrates the absence of arginase from the intestinal secretion of the dog, the conclusion being drawn that arginase is not, as is sometimes assumed, an extracellular digestive enzyme participating in the digestion of proteins in the intestinal tract. On the other hand, this enzyme occurs in the intestinal mucus of the dog or monkey, probably because it plays a part in the synthesis of homogeneous proteins from the products of digestion of heterogeneous proteins, this process being necessarily accompanied by partial destruction or elimination of certain amino acids.

J. C. S.

Autolysis of the grey matter of the brain. A. M. GEORGIEVSKAIA. *J. Russ.*

Physiol. 4, 277(1922).—During autolysis of the brain both the proteins and lipoids dissolve. After some time, however, the insol. fractions of these substances may increase owing to the formation of less sol. products. There is a considerable increase in amino N during autolysis of the brain. J. C. S.

Analogies between methylene blue and oxidases. P. A. ASCHMARIN. *J. Russ. Physiol.* 4, 283-4(1922).—Methylene blue accelerates considerably the indophenol and *p*-phenylenediamine reactions. In the former case, the velocity is augmented 5 to 10 times, and in the latter 5 to 20 times, according to the concns. of the reagents and the temp. The last-named factors exert a similar influence in the presence of methylene blue as in the presence of oxidases (cf. Vernou, *C. A.* 5, 3837; Battelli and Stern, *C. A.* 7, 819). Methylene blue may be considered as a substance analogous to the oxidases. J. C. S.

The interconversion of creatine and creatinine. IV. Origin of creatinine in the organism. AMANDUS HAHN AND GEORG MEYER. *Z. Biol.* 78, 91-118(1923); cf. *C. A.* 17, 2895.—Quant. expts. on the serum, blood, liver, and kidney of the ox and on the liver of the pig and dog show that during sterile autolysis at 38° there is no destruction either of creatine or of creatinine and no interconversion of these substances. Where occasionally an increased creatinine content was observed, it was shown to be due to the development of acidity, for, by the use of buffer mixts. of the same acidity and added creatine, a transformation into creatinine followed. Enzymes for the interconversion of creatine and creatinine or their destruction are non-existent. Similar relations hold for creatinine and creatine in urine. When creatine is taken by mouth in soln. by man, there is no increased creatinine output in the urine. Subcutaneous injections of creatine in the rabbit do not cause an increased creatinine excretion, and the whole of the creatine is excreted in 24 hrs. The origin of creatinine in man is ascribed to transformation of the creatine of muscle brought about by the reaction of the tissue. J. C. S.

Yeast and aldehyde. T. BOKORNY. *Allgem. Brauer- u. Hopfenzeit.* 1922, 1057-60, 1149-50.—A résumé is given of the work of Neuberg, Fürber, Reinfurth, von Grab and Cohen. B.'s expts. show that paraldehyde, benzaldehyde, *o*- and *p*-hydroxybenzaldehydes, and acetone do not serve as nutrient materials. Et acetate is assimilated by fungi and algae, and Et acetate gives a positive result with spirogyra if neutralized with K_2HPO_4 . A no. of carbohydrates, including pentoses, were examd. as sources of supply of C to yeast, the N being furnished by urine. With sucrose the increase in the amt. of yeast, calcd. as dry matter, is much larger with small than with large seedings and in one case amounted to 1746%. Levulose and maltose also gave considerable increases, but with lactose, rhamnose, rabinose, mannitol, and xylose the dry matter of the yeast showed marked diminution. Yeast and various substances of protein character are able to fix considerable amts. of different compds. from soln. Thus pressed yeast, with 33% of dry matter, takes up 15% of NH_3 , 20.4% of NaOH, and 1.5-7.5% of hydrazine hydrate, calcd. on the dry matter of the yeast (33%). The percentages of NH_3 fixed by blood albumin, peptone, muscle albumin, egg albumin, casein, and powd. diastase are, resp., 3.74, 0, 2.55, 4.25, 3.9, and 10.2. Diastase and peptone do not take up H_2SO_4 , but egg albumin takes up 6.37% and muscle albumin 4.9% of the acid. 20 g. of pressed yeast (with 30% of dry matter) fixes 0.9 g. of AcOH, 0.945 g. of oxalic acid, 0.072 g. of SO_2 , 0.32 g. of HF, 0.75 g. of Fuchsin, 0.34 g. of Eosin, 0.4 g. of Iodine Violet, 0.3 g. of Methyl Green, 0.5 g. of Methylene Blue, 0.3 g. of Tropæolin, 0.8 g. of Methyl Violet, 0.44 g. of Alizarin Blue, 0.6 g. of Malachite Green, 0.25 g. of Nigrosin, and 0.8 g. of Chrysoidin. In 0.5% I soln., 20 g. of pressed yeast fixes at least 0.5 g. of I. Yeast treated with CH_3O and well washed does not smell of the aldehyde, which is, however, liberated when the yeast is boiled with dil. H_2SO_4 . Salts of heavy metals may also be removed from solns. by yeast, which may possibly serve for purifying waste waters. J. S. C. I.

Precipitation of proteins (of barley) by electrolytes and its relation to degree of dispersion determined by fractional ultrafiltration. W. WINDISCH, W. DIETRICH AND A. MEHLITZ. *Wochschr. Brauerei* 40, 1-3, 7-8, 13-15, 19-21, 25-7, 31-3(1923).—The authors describe and discuss, from both chem. and phys. standpoint, the pptn. of proteins of different types from soln. by means of electrolytes. For their own expts. use was made of an aq. ext. of barley, prepd. by treating the ground grain (1 pt. of dry matter) with water (10 pts.) at a low temp. The N in the different fractions was estd. by a modification of Bang and Larsson's micro-Kjeldahl method (*C. A.* 7, 3513), the substance being oxidized by means of H_2SO_4 in the presence of a drop of Hg and the NH_3 formed distd. into 0.01 N HCl, the excess of which was estd. by titration with 0.01 N NaOH; alc. cochineal soln. served as indicator. The pptn. of the various forms of N compds. contained in the barley ext. was effected by Schjerning's method (cf.

C. A. 9, 689), the precipitants employed being SnCl_4 , HgCl_2 , ferric acetate, uranyl acetate, and MgSO_4 . The barley ext. was also subjected to fractional ultrafiltration by means of Bechhold's app. (C. A. 1, 2762), use being made of filter papers impregnated with 1.5, 3, 4.5, 6, and 7.5% solns. of collodion in glacial acetic acid and hardened with formalin; in this way, proteins of definite degrees of dispersion were sepd. from the ext. Comparison of the results obtained on examn. of the different products sepd. from the barley ext. by these two methods shows that the individual proteins obtained by Schjerning, partly by sep. pptns. and partly by combination of the products of several pptns., exhibit, not one single degree, but widely varying degrees of dispersion. The view expressed by Lüers (cf. C. A. 14, 2652) that formaldehyde reacts, not only with amino acids, but also to some extent with the free amino groups of colloidal proteins of high mol. wt., is confirmed by the observation that the proportion of N in the barley ext. which is capable of formol titration is diminished by ultra filtration of the ext.

J. S. C. I.

Influence of Kambara earth (acid bleaching earth) on certain hydrolytic enzymes. G. KITA AND K. SUZUKI. *Woch. Brauerei* 40, 79-80(1923).—Towards taka-diastase, malt-diastase, and invertase, Kambara earth exhibits the same action as an acid, although its aq. ext. is without effect. The earth may be used with advantage to activate the enzyme in technical saccharification, the subsequent neutralization required when a mineral acid is used being rendered unnecessary. The optimum acidity for the enzyme actions varies with the conditions.

J. S. C. I.

The effect of buffer salts on blood coagulation. BENJAMIN JABLONS. *J. Lab. Clin. Med.* 8, 679-81(1923).— K_2HPO_4 and KH_2PO_4 both caused a striking inhibition of blood coagulation, similar to that produced by Na citrate. The blood remained incoagulable for 48 hrs. It was bright red, like arterial blood or blood contg. oxyhemoglobin, in the case of addn. of K_2HPO_4 , and very dark red when KH_2PO_4 was added. KH_2PO_4 increased the viscosity of the blood. Hemolysis was slight with K_2HPO_4 and fairly marked with KH_2PO_4 .

E. R. LONG

Neutrality regulations in the body. D. W. WILSON. *Physiol. Rev.* 3, 295-334(1923).—A comprehensive review with extensive bibliography. The various mechanisms are considered, by which the blood is maintained at a reaction with extreme limits of p_{H} 7.05 and 7.85. Although the usual physiol. discussion lays emphasis on the fact that the kidneys aid in regulating the acid-base balance of the blood, the problem of greatest interest is just the reverse. The acid-base balance of the blood regulates urine secretion, most of the available information indicating that concn. of H^+ ions of the urine varies with that of the blood. Consideration is given to the effects of drugs, exercise, high temp., bleeding and abnormal barometric pressure.

E. R. LONG

The significance of the dual function of hemoglobin in relation to the mechanism of the chemical regulation of respiration. ROBERT GESELL. *Proc. Am. Physiol. Soc., Am. J. Physiol.* 63, 393-4(1923).—In certain conditions there may be a broken coordination of the dual function of hemoglobin, viz., carrier of O_2 and source of alk. to the plasma, with abnormal breathing resulting. The respiratory center may respond to changes in acidity resulting from its own metabolism (vanguard of internal respiration) or to changes in acidity of the circulating plasma resulting from the metabolism of the body as a whole (rear guard of internal respiration). Hyperpnea following hemorrhage, the effect of CO_2 administration on hyperpnea of O_2 want and on the hyperpnea and convulsions of excess O_2 are briefly discussed.

J. F. LYMAN

Chemical effects produced by passing electric currents through thin artificial membranes of high electrical resistance. R. S. LILLIE AND S. E. POND. *Proc. Am. Physiol. Soc., Am. J. Physiol.* 63, 415-6(1923).—An elec. current corresponding to a potential of 10 v. flowing across a rubber membrane of 40 μ thickness interposed between 2 electrolyte solns., one of which is a mixt. of FeCl_3 and KSCN , causes oxidation of Fe^{++} to Fe^{+++} . Oxidation occurs at the surface of the membrane facing the cathode.

J. F. LYMAN

The concentration of protein in tissues. E. J. COHN. *Proc. Am. Physiol. Soc., Am. J. Physiol.* 63, 430-1(1923).—The relationship of H_2O , electrolytes and proteins in animal tissues is discussed from the standpoint of phys. chemistry. The variations among species of these cell constituents agree with the theories of Donnan and of Loeb on membrane equil. The concn. of such dissociable, non-diffusible contents of cells as the proteins must lead not only to the loss of H_2O , but also to the loss of diffusible electrolytes with which the proteins are in equil.

J. F. LYMAN

The chemical regulation of the activities of the human kidney. E. F. ADOLPH. *Proc. Am. Physiol. Soc., Am. J. Physiol.* 63, 432-3(1923).—Hypertonic solns. of substances not changed in metabolism (e. g., sucrose) caused excessive excretion of H_2O

by the kidneys; but only the substance ingested was excreted in this excess of H_2O at a rate much above normal. Drinking water alone caused a diuresis in which very little except H_2O was excreted at more than the normal rate. Locke's soln. and isotonic $NaCl$ gave no true diuresis but a slightly augmented H_2O excretion lasting many hrs. Isotonic solns. and KCl and urea, on the other hand, induced very rapid diuresis. Isotonic $CaCl_2$ solns. produced no increment in H_2O excretion, possibly due to inhibition in the permeability of the kidney. J. F. LYMAN

Heparin, an anticoagulant. W. H. HOWELL. *Proc. Am. Physiol. Soc., Am. J. Physiol.* 63, 434-5(1923).—An improved method of prep. heparin (*C. A.* 13, 750) is described. One mg. in saline soln. added to 5 to 10 cc. of blood outside the body prevents clotting. Injected intravenously in this proportion heparin renders the blood incoagulable with no other noticeable effect upon the animal. J. F. LYMAN

Influence of temperature upon the action of the testicular hormone. M. ARON. *Compt. rend.* 177, 141-3(1923).—Tritons (species not stated), freshly collected with sexual characters fully developed, were castrated and placed in water at varying av. temps. Those maintained at an av. of 23° became completely regressed in sexual characters in 14 days; those at 14° required 21 days. Of the third lot maintained at 7° , two were killed at the end of 14 days and their internal characters were not different from those of normal controls. After 28 days 2 more were killed in which a small beginning of retrogression was noted. The remaining specimen at the end of 35 days still showed a very sinuous Wolff canal and the brilliant silver band. It appears that the temp. acts upon the residual hormone after castration. The testicular hormone behaves as a substance subject to chem. dynamism. L. W. RIGGS

Demonstration of the presence of sucrose in the walls of the mucoid cysts of the ovary. P. LECÈNE AND H. BIERRY. *Compt. rend.* 177, 222-4(1923).—This study is mainly histological. Macerations of fragments of the walls of 2 typical mucoid cysts of the ovary were made in the ordinary way in the presence of toluene and thymol, and in vessels of Pyrex glass. The p_H of the macerations was 6.2. These macerations were able to decomp. in 48 hrs. 60 to 80% of sucrose added thereto in concns. of 2 to 4%. Expts. with controls and with other cysts failed to show a trace of sucrose. It is concluded that in certain cases the wall of the mucoid cyst of the ovary, covered by cylindrical epithelium rich in cup-formed cells, and which present morphological analogies to the fetal intestinal lining, may contain an active sucrose similar to the diastase of the intestinal wall. L. W. RIGGS

Unrecognized factor in altitude effects. WITHROW MORSE. *Sci. Monthly* 17, 108-13(1923).—From observations at 10,000 ft. in the Wet Mts. of Colo. and from the experience of mountain climbers the question is proposed: Can the organism take care of the acids formed while there is not enough supply of alkali reserve to take care of the additional dangerous acids (lactic, acetylacetic and hydroxybutyric)? This question is discussed with reference to O supply as modified by altitude, temp., sunlight and air movements. Stagnant air at comparatively low altitudes, especially in the sunlight, causes more discomfort than lively air at much higher altitudes. L. W. RIGGS

The composition of thymic acid. R. FEULGEN. *Z. physiol. Chem.* 128, 154-61(1923).—The chem. identity of thymic acid is maintained and some misconceptions of Thannhauser and Ottenstein (*cf. C. A.* 16, 278) are pointed out. R. L. STEHLER

Natural porphyrins. I. The porphyrin of *Eisenia fetida*. H. FISCHER AND O. SCHAUMANN. *Z. physiol. Chem.* 128, 162-6(1923). II. Turacin. H. FISCHER AND J. HILGER. *Ibid* 128, 167-74(1923).—A preliminary communication. The pigment apparently belongs in the urinoporphyrin series. R. L. STEHLER

Hemoglobin. I. H. FISCHER AND K. SCHNEIDER. *Z. physiol. Chem.* 128, 230-9(1923).—When 2,4-dimethyl-3-carboxyoxypyrrrole in pyridine was heated with $AcCl$ at 50° a mol. compd. contg. 2 mols. of the pyrrole deriv. and 1 mol. of pyridine pptd. which m. $173-4^\circ$. R. L. STEHLER

Lactic acid fermentation of glucose by peptone. An experimental testing of the results of G. Schlatter. CHR. BARTHEL AND H. V. EULER. *Z. physiol. Chem.* 128, 257-83(1923); *cf. Schlatter, C. A.* 17, 280.—Schlatter's results were probably due to bacterial contamination. When the expts. are conducted aseptically no lactic acid is formed. R. L. STEHLER

Hemicelluloses. III. The fermentative hydrolysis of lichenin. HANS FRINGS-SHREIN AND KARL SEIFERT. *Z. physiol. Chem.* 128, 284-9(1923); *cf. C. A.* 17, 2270.—Pure lichenin from Iceland moss gives only glucose on treatment with malt amylase. At the optimum reaction $p_H = 5$. R. L. STEHLER

Filtration through frog skin. TORALD SOLLMANN. *J. Pharmacol.* 21, *Proc.* 200-1(1923).—The sacs formed by stripping the skin from the hind legs of frogs are used to

study the phenomena of filtration through a relatively simple living tissue; the changes are much more marked in the living than in the dead skin. The rate of filtration (as compared with 0.75% NaCl) is quickened by hypertonic solns. and by isotonic alkali, acid (0.001 *N*) and Ca precipitants (oxalate, fluoride, citrate). It is slowed by distd. H_2O . No definite effect is obtained by quinine to 1:1000 and by tannin to 0.5%.

C. J. WEST

Electrical properties of gels (MICHARD) 2.

KOPACZEWSKI, W.: *Théorie et pratique des colloïdes en biologie et en médecine*. Paris: Vigot Frères. 308 pp. Reviewed in *Physiol. Abstracts* 8, 161(1923).

MACLEOD, J. J. R. *et al.*: *Physiology and Bio-chemistry in Modern Medicine*. 4th Ed. Revised and enlarged. St. Louis: C. V. Mosby Co. 243 pp. \$11.

OSTERHOUT, W. J. V.: *Injury, Recovery and Death, in Relation to Conductivity and Permeability*. Philadelphia and London: J. B. Lippincott Co. 259 pp. \$2.50. Reviewed in *J. Am. Chem. Soc.* 45, 1861(1923).

PETERS, FREDUS N.: *Chemistry for Nurses*. 2nd Ed. Revised. St. Louis: C. V. Mosby Co. 302 pp. \$2.50.

B—METHODS AND APPARATUS

STANLEY R. BENEDICT

Investigations of a "germination method" for the detection of silver in a section of tissue. R. ED. LIESEGANG AND W. RIEDER. *Z. wiss. Mikroskopie* 38, 334-8(1922); *Chem. Zentr.* 1922, 111, 567-8; cf. *C. A.* 6, 637.—Microtome sections of any kind of tissue can be impregnated with Ag by the method of Ramon y Cajal if to the hydroquinone (which follows the $AgNO_3$ impregnation) is added gum arabic as a protective colloid. The pptn. of metallic Ag in the tissue does not occur if Ag nuclei have not formed through long contact of the tissue with $AgNO_3$. This method, which heretofore has been applied only to cerebral tissue, is used for verifying the results of Voigt (cf. *C. A.* 9, 1512) that after intravenous injection of rabbits with colloidal Ag the latter can be found in the epithelia of the urethra. Voigt came to this conclusion because he observed particles by the ultramicroscope which disappeared on treatment with KCN. Such particles upon treatment with a freshly prepd. mixt. of $AgNO_3$, hydroquinone and gum arabic probably act similarly to the development of Ag nuclei in photography. Since no deposition of metallic Ag was found in microtome sections of the kidneys of rabbits which had undergone intravenous injection of colloidal Ag, it is concluded that colloidal Ag is not deposited in the epithelia of the urethra.

C. C. DAVIS

Some observations on the detection of acetone in urine. B. A. VAN KETEL. *Pharm. Weekblad* 60, 833-6(1923).—In making the color test for MeAc by means of Na nitroprusside and NH_4OH , the NH_4OH should first be tested since it often contains traces of MeAc. $MeCHOHCH_2CO_2H$ does not give the nitroprusside reaction.

A. W. DOX

The hydrogen-ion concentration of different kinds of glassware when sterilized with buffered and nonbuffered solutions. F. W. FABIAN. *Mich. Sta. Rept.* 1921, 173-8; *Expt. Sta. Record* 48, 204.—Data are reported from a study by R. C. Stull of the changes in the H-ion concn. of buffered and nonbuffered solns. when sterilized in soft and hard glassware. For the nonbuffered soln. triple distd. water was used and for the buffered soln. a standard nutrient broth, both being adjusted to $p_H = 7$. The detns. of H-ion concn. following the different treatments were made colorimetrically with the Clark and Lubs indicators in a Cooledge comparator. The glassware included soft glass tubes, hard glass tubes, 4-oz. druggists' bottles, Erlenmeyer flasks, Kolbe flasks, and Smith fermentation tubes. Each kind of glass was divided into 3 sets. One consisted of new unwashed glassware. This was filled with the nonbuffered cond. water and autoclaved for 30 min. at 15 lbs. pressure and cooled, after which a 10 cc. sample was taken and its p_H value detd. The same glass was then refilled 4 times with nonbuffered cond. water and twice with broth, autoclaved after each time, and the p_H value detd. A second series was run with the same kind of glassware, the cond. water being used 6 times and the broth twice. In the third set the glassware was first filled with cleaning soln., heated 30 minutes in flowing steam, rinsed 5 times in tap water and once in distd. water, after which it was treated as in the first set of expts. Tabulated results showed that glassware taken from stock and filled with a nonbuffered soln. yielded enough alkali during autoclaving to change the reaction from $p_H 7$ to $p_H 9.8$. The amt. of alkali yielded by the same glass was not sufficient, however, to change the reaction of the buffered soln. during autoclaving. The soft glass yielded more alkali on autoclaving than did the hard glass. Treatment of the glass with cleaning soln. did not prevent

its giving off alkali on autoclaving, but appeared to destroy or neutralize the substances that in some tests interfered with the action of the indicator. The practice of treating new glassware with cleaning soln. before use is recommended on this account. H. G.

A method of estimation of diastase in blood. G. M. FYFE. *Brit. J. Exptl. Pathol.* 4, 127-31 (1923).—By an adaptation of Maclean's (C. A. 13, 2889) method of blood sugar estn., a simple and accurate method has been evolved which permits of an almost concurrent reading of the blood sugar and the blood diastase figures, while only a small amt. of blood is required. The final result depends on a detn. of the patient's blood sugar by Maclean's method, and on a 2nd detn. after 0.2 cc. of the patient's blood has been incubated for $\frac{1}{4}$ hr. at 37° with 1 cc. of a 0.1% soln. of starch. The result is calcd. as the % of sol. starch transformed to sugar (calcd. as glucose) by the 0.2 cc. blood employed. The amt. of starch used is 1 mg., and the difference between the sugar contents, measured in fractions of a mg., of the 2 samples of 0.2 cc. blood will be equiv. to the amt. of starch reduced to sugar. HARRIET F. HOLMES

The preservation of ox gall. H. LÖFFLER. *Oesterr. Chem. Ztg.* 26, 92-3 (1923). Ox gall may be protected from bacterial decompn. by treating the concd. soln. with SO_2 . I. P. ROLF

The calculation of a respiration experiment according to the Zuntz-Geppert principle. W. KLEIN AND M. STEUBER. *Biochem. Z.* 136, 471-6 (1923).—A simpler method of calcn. is proposed. A table of factors is given. GEORGE ERIC SIMPSON

The determination of oxygen utilization in a respiration experiment carried out with the Pettenkofer-Tigerstedt apparatus. W. KLEIN AND MARIA STEUBER. *Biochem. Z.* 136, 477-81 (1923).—Even in a large app. O_2 can be detd. with as high a degree of accuracy as CO_2 . An expt. with alc. is reported and calcn. are shown. GEORGE ERIC SIMPSON

Apparatus for biological gas analysis. F. BRAMICK. *Biochem. Z.* 137, 53-9 (1923).—The Hempel "app. for exact gas analyses with Hg merely as a trap fluid" is modified to promote ease and surety of manipulation. GEORGE ERIC SIMPSON

The determination of the hydrogen pumber in blood. F. BRAMICK AND R. COHET. *Biochem. Z.* 137, 60-6 (1923).—A procedure is described by which air samples of a desired CO_2 tension can be prepd. GEORGE ERIC SIMPSON

The ferricyanide method for blood sugar. II. H. C. HAGEDORN AND B. NORMAN JENSEN. *Biochem. Z.* 137, 92-5 (1923); cf. C. A. 17, 2721.—Uric acid and creatinine increase reduction as measured by the Hagedorn method. β OHIC₁₂H₃CO₂H and Me_2CO do not. GEORGE ERIC SIMPSON

Some clinical-chemical methods. II. CITRON. *Biochem. Z.* 137, 96-101 (1923).—Some new dodges in the hypobromite blood urea, Kjeldahl, and in the NH_3NHCl method for urinary Me_2CO , also in gastric analysis, are described. Cf. C. A. 17, 1813. GEORGE ERIC SIMPSON

The quantitative estimation of neosarsphenamine and its absorption by bacteria and body cells. E. REMY. *Biochem. Z.* 137, 133-43 (1923); cf. C. A. 17, 1073. Neosarsphenamine is taken up from physiol. NaCl soln. in appreciable amts. both by bacteria and liver cells. It is adsorbed. From serum adsorption is about 50% as great. The following method for detg. neosarsphenamine was developed: To each 100 cc. of urine add 1 cc. of a soln. contg. 20 g. NaOH plus 20 g. KOH per 100 cc. Filter. To each 5 cc. of clear filtrate add, with cooling in an ice bath, 10 drops 10% HCl plus 5 drops 1% NaNO_2 . A red color is produced by adding a few drops of strongly alk. resorcinol soln. which is compared with a 1:5000 soln. (or other convenient diln.) of neosarsphenamine similarly treated. The urine should not stand over 1 hr. Error about 2%. GEORGE ERIC SIMPSON

Nephelometric apparatus and the technic of nephelometric procedure. HANS KLEINMANN. *Biochem. Z.* 137, 144-56 (1923).—A modification of Kleinmann's nephelometer (C. A. 14, 2357) is illustrated. It is designed for micro- as well as macro-nephelometry. Some of Weinberg's criticisms (C. A. 16, 944) are answered. A method of prepg. standards is described, following the suggestion of Bechhold (C. A. 17, 659). Remarks on the use of the nephelometer are appended. GEORGE ERIC SIMPSON

A method for the nephelometric determination of small amounts of calcium. P. RONA AND H. KLEINMANN. *Biochem. Z.* 137, 157-83 (1923).—Take up ash contg. 0.04 to 0.4 mg. Ca in 3 (not over 6) drops N HCl , and make alk. with 5 to 6 (not over 30) drops $\text{N NH}_4\text{OH}$. Dil. to about 5 cc. (1 to 12 cc.) and add 0.4 cc. reagent. After 3 min. dil. to 25 cc. and compare with a suitable standard. Reagent: 10 cc. Merck's Na sulfocinate in 112 cc. N NaOH dild. to 125 cc. In prepg. reagents and making dilns. fresh cond. H_2O is used. This procedure is subjected to extended exptl. analysis with aq. Ca solns. Error 1%. It is suggested that 1 cc. blood should suffice for a

detn., or, if the micro-nephelometer (see preceding abstr.) be used and the final diln. reduced, 0.25 cc. should suffice. Ca may be pptd. with oxalate to sep. it from Mg which is included in this detn. Possibly in blood detns. this may be dispensed with, since here Mg is small and probably const. in amt.

GEORGE ERIC SIMPSON

A micro-method for the determination of total phosphorus in blood and feces. WERNER GROTE. *Z. physiol. Chem.* 128, 254-6(1923).—After ashing the P is pptd. as ammonium phosphomolybdate and the N content of the ppt. detd. by the Kjeldahl method.

R. L. STEHLE

New process for the volumetric estimation of NH_3 and carbamide N by the hypobromite method (TILLMANS, KRÜGER) 1.

ABDERHALDEN, F.: *Handbuch der biologischen Arbeitsmethoden—Methoden zur Erforschung der Leistung des tierischen Organismus, Methoden der zoologischen Forschung.* Berlin und Wien: Urban und Schwarzenberg. Pp. 439-584. 6.3 Swiss francs.

C—BACTERIOLOGY

A. K. BAILS

Intestinal bacteria. VI. Biology of the intestinal flora of the newborn; nutritional properties. A. ADAM. *Z. Kinderheilk.* 33, 308-12(1922); cf. *C. A.* 17, 788.—In the meconium the Gram-positive spore-bearing bacterium of *Escherich* is almost uniformly to be found up to the time that *B. bifidus* appears. It then disappears, evidently because the environmental conditions become unsuited to its growth. Since the intestinal flora is detd., in part, by the character of the food supply the reactions of this organism described by *Escherich* to various food substances were detd. Growth was not affected by urea, glyccol, alanine, leucine, or tyrosine. Asparagine slightly stimulated growth. In biuret-free peptone luxuriant growth took place with the formation of gas, but no indole. Na caseinate did not modify growth. Of the neutral fats triolein was inert, tributyrin was inhibitory. Glycerol had no effect; oleic acid restricted growth. Na and Ca oleinate prevented growth; Na and Ca lactate were inactive. AcH , pyruvic acid, and its Ca salt inhibited, while the Na salt favored, multiplication. Acid and gas were formed from glucose, galactose, levulose, saccharose, maltose, and lactose; and the morphology of the organisms was somewhat affected by the type of sugar used. Dextrin slightly favored growth; starch was without effect. Hematin was without influence. These activities correlate well with the chem. compn. of the food material present in the meconium.

G. H. S.

The effect of change in type of intestinal bacteria on urinary indican and phenols. A. H. SMITH AND W. L. KULP. *Proc. Soc. Exptl. Biol. Med.* 20, 44(1922).—Intestinal implantation of *B. acidophilus* resulted in no significant changes in urinary indican and combined phenols.

C. V. B.

The influence of diet and of *Bacillus acidophilus* ingestion on intestinal putrefaction. L. KAST, J. J. SHORT AND H. M. CROLL. *Proc. Soc. Exptl. Biol. Med.* 20, 45-6(1922).—In man, indican in the urine paralleled the intake of animal protein; phenols as detd. by the method of Folin and Denis showed no significant changes. Implantation of *B. acidophilus* in the intestinal tract did not decrease putrefractive changes as indicated by the excretion of indican in the urine.

C. V. B.

Testing and evaluation of disinfectants. E. HALLER. *Z. angew. Chem.* 36, 423-7(1923).—See *C. A.* 17, 206.

W. O. E.

Action of mercuric chloride on bacteria. H. ENGELHARDT. *Desinfection* 7, 63-5, 81-3(1922).— HgCl_2 is absorbed by the outer membrane of bacteria, thereby preventing reproduction, and can usually be removed by prolonged washing of the bacteria with water, or, where treatment with the HgCl_2 has been more vigorous, by treatment with absorbents such as charcoal, or by decompn. of the HgCl_2 by the action of sulfides. The suggestion that sulfides decompose a Hg-protein compd. formed in the interior of the bacteria is not feasible; the action of sulfides, like that of charcoal, merely removes adsorbed HgCl_2 . *Staphylococci* which have been treated for 8 hrs. with 0.1%, or for 2 hrs. with 1.0% solns. of HgCl_2 , and anthrax spores which have been treated at 18° for 14 days with 5% solns. show signs of life after washing with water; *staphylococci* which have been treated for 72 hrs. with 1.0% solns. can be rendered capable of reproduction by treatment with sulfides; while anthrax spores which have been treated at 37° for 35 days with 0.1%, 25-33 days with 1.0%, 13-20 days with 3%, or 11-17 days with 5% HgCl_2 solns. can be revived by treatment with charcoal or sulfides. HgCl_2 cannot therefore be described as a disinfectant with a rapid direct action.

J. S. C. I.

Final hydrogen-ion concentration in the paratyphoid enteritidis group. ETSUO

YURI. *J. Infectious Diseases* 32, 479-80(1923).—The several types of paratyphoid enteritidis bacilli cannot be differentiated from one another or from the typhoid bacilli by the final H-ion concn. in dextrose broth cultures. The pH varies within narrow limits (4.6-6.9).

JULIAN H. LEWIS

The action of several diuretics on bacteria. KARL BAUER. *Centr. Bakt. Parasitenk.*, I Abt. 90, 42-8(1923).—The diuretics, urea, caffeine Na salicylate, caffeine Na benzoate, and theobromine Na salicylate, when added to neutral agar in concns. of 2 to 5% either inhibit or destroy the growth of many bacteria. When added to completely developed cultures or a suspension of bacteria the organisms are not dissolved but their vitality is markedly lowered.

JULIAN H. LEWIS

The value of the potato starch-peptone broth of Kodama and Takeda in the diagnosis of cholera. E. GILDEMEISTER AND KURT HERZBERG. *Centr. Bakt. Parasitenk.*, I Abt. 90, 53-5(1923).—It is shown that all cholera vibrios do not form a diastatic enzyme which digests starch as claimed by Kodama and Takeda (C. J. 17, 119) and that other organisms may digest starch as completely as the cholera vibrios. The practical use of this medium for the diagnosis of cholera is therefore limited. J. H. L.

The pigment formed by two strains of *B. xerosis*. WILHELM ROTHER. *Centr. Bakt. Parasitenk.*, I Abt. 90, 127-8(1923).—A red pigment is formed only in the presence of dextrose. The optimum temp. is that of the incubator. The pigment is sol. in $CHCl_3$ and alc., but is not sol. in ether and H_2O .

JULIAN H. LEWIS

Studies in bacterial metabolism. XLIV-LVI. A. I. KENDALL, A. A. DAY AND A. W. WALKER. *J. Infectious Diseases* 30, 141-210(1922). LVII. A. I. KENDALL. *Ibid* 211-24. LVIII-LXI. A. I. KENDALL AND R. C. HANER. *Ibid* 225-38. LXII. A. I. KENDALL AND R. S. BLY. *Ibid* 239-44. LXIII. A. I. KENDALL, R. C. HANER AND R. S. BLY. *Ibid* 245-7. LXIV. A. I. KENDALL AND A. A. DAY. *Ibid* 248-50. LXV. A. I. KENDALL, H. C. CHEETHAM AND C. S. HAMILTON. *Ibid* 251-8. —A mass of information is presented on the N and carbohydrate metabolism of a large no. of bacteria. Quant. detns. are made of total N, non-protein N, NH_3 N, NH_4 N and the effect of various carbohydrates on these as well as on other products of bacterial growth such as toxins and proteolytic enzymes. Cf. following abstr. JULIAN H. LEWIS

Bacterial metabolism. A. I. KENDALL. *Physiol. Rev.* 3, 438-55(1923). cf. preceding abstr.—A review with bibliography. Bacteria are essentially transformers, not accumulators of energy. Each microbe exhibits a remarkable specificity of chem. action, which is useful for its identification. Especial attention is devoted to the protein-sparing action of the carbohydrates, and the effect of the presence of carbohydrate upon the products formed from protein. E. R. LONG

The action of chemicals on gonococci in vitro and in vivo. K. W. JÖTTEN AND C. PASCH. *Z. Hyg.* 98, 161-73(1922).—Ag prepn., $HgCl_2$ and its compds., as others have shown, are the most active in killing gonococci. The addition of small amts. of dyes, terpinchin, terpene, etc., did not influence the action of Hg compds. The action of these substances was detd. both by culture and by injecting intraperitoneally into mice. Hg compds., especially $HgCl_2$, and argoiflavine are active when all other substances fail. JULIAN H. LEWIS

The influence of temperature increase on the surface tension of different bacteria. M. TINTRI. *Z. Immunitäts.* 36, 337-46(1923).—Gildemeister's findings (*Centr. Bakt. Orig.* 83, 497(1919)) with respect to the effect of heat upon the surface tension of typhoid bacilli, viz., increase at 80° and decrease at 100° , represent no const. condition. Bacterial surface tension varies considerably in its response to heat in different strains. In a single strain the findings show great variation. In general, heating *B. paratyphoid* B. caused a progressive decrease in surface tension. Heating colon bacilli, dysentery bacilli and staphylococci up to 100° for the most part was without influence upon surface tension. Beyond 100° a marked lessening of surface tension occurred. Heating a strain of *B. proteus* caused a lowering of surface tension, which was progressive up to 142° , and then became much more marked. Friedländer bacilli showed a const. decrease. Diphtheria bacilli were scarcely affected. *B. subtilis* showed a progressive decrease. *B. mesentericus* behaved in varying fashion. Suspensions of beer yeast showed first a decrease in surface tension, then an increase, and finally a sharp decrease. The results with baker's yeast were less significant. The addn. of an agglutinating serum to OX19 and typhoid bacillus suspensions had no recognizable influence on surface tension. All measurements were made with the stalagmometer. E. R. LONG

Investigation of the agents of toxic gangrene. I. Toxin formation by the Foth type, and the toxicologic, immunizing and biochemical properties of the toxin. KATSUMI KOJIMA. *Z. Immunitäts.* 37, 170-84(1923).—The Foth type of the gas gangrene

bacillus produces in suitable media, particularly Martin broth enriched with coagulated egg white, a toxin which is fatal for mice and guinea pigs intravenously, and in sufficient amt. subcutaneously. In the Berkefeld filtrate from the culture flask 2 different substances are found, one causing death, and the other causing hemolysis. The true toxin and the hemolysin are both thermostable, being destroyed at 52° for 30 min., and are both difficultly dialyzable. The hemolysin is completely salted out by half satn. with $(\text{NH}_4)_2\text{SO}_4$; the true toxin remains in the fluid uninfluenced. Pepsin and trypsin attack both. II. Toxin and antitoxin of the Foth and Kitt types and their special differences. *Ibid* 37, 185-202(1923).—The Foth and Kitt types of gas gangrene bacillus are hard to distinguish morphologically or by agglutination. They can be sepd. on the basis of biochem. properties. For the Kitt strain a considerable amt. of sugar in the medium is necessary (0.5-3%), while for the Foth strain sugar is unnecessary or harmful. Toxin production by the Kitt strain occurs on a great variety of sugar media, while with the Foth strain it is observed only in special media. The Kitt type forms a sp. toxin neutralized only by Kitt antitoxin. Kitt antitoxin has no particular effect upon Foth toxin. Foth toxin is not very strong, but is influenced only by Foth antitoxin. The respective hemolysins are neutralized only by the sp. immune serums. Immunization of an animal against gas gangrene by means of a non-toxic filtrate occurs with the Foth type, but not with the Kitt type.

E. R. LONG

Activation of the formation of poisonous substances by *Bacillus emphysematosus* of Fränkel by means of catalysts. KATSUMI KOJIMA. *Z. Immunitäts.* 37, 203-10 (1923).—Phenanthraquinone and colloidal S, which Neuberg showed to be activators for the sugar fermentation of yeast, increase the production of poisonous substances by the Fränkel bacillus. Cf. C. A. 16, 1967.

E. R. LONG

Agglutination of bacteria by dyes. G. A. BROSSA. *Z. Immunitäts.* 37, 221-7 (1923).—Colon and typhoid bacilli and cholera vibrios, all carrying a negative charge, are agglutinated by basic dyes. A low concn. of dyes is noticeably effective with the cholera vibrio. No sp. action of various dyes is found.

E. R. LONG

Bacterial poison, especially the dry typhoid bacillus poison, and its therapeutic use. V. MASAOKI YOSHIOKA. *Z. Immunitäts.* 37, 249-84(1923); cf. C. A. 17, 2501.—A 3 weeks broth typhoid bacillus culture is satd. with $(\text{NH}_4)_2\text{SO}_4$ and the pptd. mass dialyzed for some days, centrifuged and dried in the Faust-Heim evapn. app. The prepn. is a yellowish gray, odorless, tasteless powder, sol. in water, insol. in Et_2O , EtOH and CHCl_3 . It is acid and contains protein. The lethal intravenous dose for 250 g. guinea pigs is 0.015-0.011 g., the poison acting with marked rapidity. For rabbits the lethal dose is 3-4 times that for guinea pigs, for mice 7 times. Mice are thus relatively resistant. The poison can be prepd. from protein-free media. It consists of a labile portion, which disappears in 9 days at 10° and 30 min. at 90°, and a stable portion destroyed at 120° for 30 min. Guinea pigs immunized against this typhoid bacillus poison are resistant to further doses of the poison and to the bacilli themselves. On the other hand treatment of guinea pigs with typhoid bacilli does not protect against the poison. The protective effect is sp.; no immunological relationship with the colon bacillus and cholera vibrio poisons can be noted. Y. is able favorably to influence the clinical course of typhoid fever in man with small doses of the poison.

E. R. LONG

The bacteriostatic and selective action of gentian violet and other alkaline dyes. J. W. CHURCHMAN. *Chimie et industrie* 10, 212-5(1923).—Brief review, mostly of C.'s work. (See C. A. 16, 948, 2880; 17, 788.)

A. PAPINEAU-COUTURE

The lysozyme effect. ONARI NAKAMURA. *Wiener klin. Wochschr.* 36, 322-3 (1923).—The so-called "lysozyme action" was described by A. Fleming as the sp. lytic effect of tears, nasal secretion and of other body fluids and tissues upon certain saprophytic bacteria, especially upon the sarcinae of the air. Heavy suspensions of the latter are clarified (dissolved) by lysozyme action in a short time. Similar action by leucocytes had been previously described by Weil and by Suzuki. Increase of temp. up to 45° has an accelerating effect upon the lytic action. Different microorganisms vary in their susceptibility from easy soly. to almost complete insol. All of the human pathogens tried were completely insol. The lysozyme action of tears and egg white persists up to dilns. of 1:100,000, and it resists heating up to 75°. Tears may be boiled for a short time and retain traces of the sp. effect. The lytic action is effective in physiol. salt soln., beef broth, or solid media, and is not inhibited by gelatin as bacteriophage action is. Susceptible organisms retain their susceptibility after careful killing and boiling. The ordinary antiseptics in not too great concns. have no inhibiting effect. A striking similarity to the Danysz phenomena is found in the lysozyme action, inasmuch as a given quantity of lysozyme-contg. fluid will dissolve a large amt. of a bacterial

suspension, if the latter be added in small portions, but it will not completely dissolve the same amt. if it is added at once. It was not found possible to cultivate a strain of lysozyme-fast sarcinae. The reaction of the medium exercises its effects within rather wide limits: the accelerated lysozyme action in $N/8000$ HCl did not diminish until the HCl concn. was increased up to $N/2000$. In more acid media the action was retarded, but it was reaccelerated when neutralized. The retarding or destructive effect of excessive OH concn. is permanent, and is not abolished on neutralization.

W. A. PERLWING

Effect of humus in weak and in strong doses upon the fixation of nitrogen by *Azotobacter chroococcum*. J. VOICU. *Compt. rend.* 176, 1421-3(1923); cf. C. A. 16, 3676.—Tests were made using 0.1 to 5.0 mg. of humus per 100 cc. of a 2% sucrose liquid culture, also using 100 to 200 mg. per 100 cc. Five mg. per 100 cc. caused 3 times as much N to be fixed as in the control without humus; 100 and 200 mg. of humus increased the amt. of N by 7 and 9 fold, resp. The sucrose consumed and the amt. of N fixed per g. of sucrose rise with the amt. of humus added.

L. W. RIGGS

Production of β -hydroxybutyric acid by certain bacteria of the *B. subtilis* group. LEMOIGNE. *Compt. rend.* 176, 1761-3(1923).—*B. subtilis* was grown on meat bouillon gelose, sweetened and alk. to litmus. After 3 to 4 days the bacteria were suspended in a sterile water or mineral medium when the suspension rapidly became acid so that in 24 hrs. its acidity was equiv. to about 1 g. H_2SO_4 per l. and was caused by the presence of β -hydroxybutyric acid.

L. W. RIGGS

The production of mercaptan from *l*-cystine by bacteria. MASATOSHI KONDO. *Biochem. Z.* 136, 198-202(1923).— H_2S and Et_3S are formed from cystine by both *B. coli* and *P. vulgaris*. Mercaptans are not produced by *B. coli*. *P. vulgaris* forms mercaptans in the presence of glucose, lactose, sucrose, glycerol and histidine, but not in the presence of glycocoll, *d*-alanine, *l*-leucine, *l*-tyrosine and *d*-glutamic acid. Perhaps a substance is formed by fermentation of the added sugar which is necessary for mercaptan production. These conclusions are based on the analysis of culture media containing the substances mentioned.

GEORGE ERIC SIMPSON

The absorption of trypanflavine by dead bacteria. LEO BLYVER. *Biochem. Z.* 136, 392-402(1923).—The bacteria were killed (a) by heat, or (b) by $CHCl_3$, Et_2O or $EtOH$. The dead bacteria were suspended in physiol. salt soln. The ability of such suspensions to take up trypanflavine was detd. Surface tension measurements were sometimes made. No generalization is possible from the results obtained.

GEORGE ERIC SIMPSON

The influence of plant lipases on the *Mycobacterium tuberculosis* poikilothermorum L. N. T. KORINEK. *Biochem. Z.* 136, 530-6(1923).—With the autolysis of living Friedmann's *Mycobacterium* in H_2O or in lipase solns., an acid reaction develops. This is not responsible for the autolysis. In weak lactic acid soln. autolysis is slower than in H_2O . In 2% lactic acid the bacteria are preserved for a long time, involution forms developing. This explains the finding of living tuberculosis bacilli in old tubercular lungs. Since on hydrolysis in aq. soln. the acid-fast and Gram-positive properties are lost, and since lipase does not dissolve the bacteria, which, however, lose their acid-fast character and are no longer Gram-positive, therefore these properties are not to be ascribed to the presence of an easily hydrolyzable lipid. Ricinus lipase was used.

GEORGE ERIC SIMPSON

Soluble specific substance of pneumococcus. M. HEIDELBERGER AND O. T. AVERY. *J. Exp. Med.* 38, 73-9(1923).—The process for the isolation of the sol. sp. substance of pneumococcus consists in the concn. of the broth, pptn. with $EtOH$, repeated resoln. and repptn., followed by a careful series of fractional pptn. with $EtOH$ or $AcMe$ after acidification of the soln. with $AcOH$ and finally, repeated fractional pptn. with $(NH_4)_2SO_4$ and dialysis of the aq. soln. of the active fractions. The yield from 75 l. of broth averages about 1 g. The material obtained by this method consists mainly of a carbohydrate which appears to be a polysaccharide built up of glucose mols. Whether the sol. sp. substance is actually the polysaccharide, or occurs merely associated with it, is still undecided, although the evidence points in the direction of the former possibility.

C. J. WEST

Enzymes of pneumococcus. IV. Bacteriolytic enzyme. O. T. AVERY AND GLENN E. CULLEN. *J. Exp. Med.* 38, 199-206(1923); cf. C. A. 15, 544.—Pneumococci possess an active intracellular enzyme which causes lysis of heat-killed pneumococci of the same and heterologous types and to a less degree of the closely related organism, *Streptococcus viridans*. The optimum reaction for lysis lies between pH 6 and 8. The bacteriolytic action is proportional to the concn. of the enzyme. Heat-

ing the enzyme to 60° for 30 min. destroys its activity. The possible relation of the enzyme to autolysis is discussed.

C. J. WEST

Bacterial nutrition. IV. Effect of plant tissue upon growth of pneumococcus and streptococcus. H. J. MORGAN AND O. T. AVERY. *J. Exptl. Med.* 38, 207-17 (1923); cf. *C. A.* 15, 3658; 16, 948.—The initiation of active growth in broth cultures of pneumococcus, *Streptococcus hemolyticus* and *S. viridans* is accelerated by the presence of unheated plant tissue. Cultures of pneumococcus in broth contg. unheated plant tissue show a prolongation of the stationary phase of growth. Death of the individual organisms in pneumococcus broth cultures contg. such tissues does not proceed so rapidly as in cultures without the tissue. The zone of H-ion concn. within which growth of pneumococcus on ordinary broth can be initiated is considerably extended, both on the acid and on the alk. side, by the addn. of unheated vegetable tissue to the media.

C. J. WEST

Oxidation of S by microorganisms in black alkali soils (Waksman, *et al.*) 15. Influence of the H-ion concentration on the growth and fixation of N by cultures of *Azotobacter* (GAINY, BATCHELOR) 15. Sugar contained in tuberculinic acid, the nucleic acid of tubercle bacilli (BROWN, JOHNSON) 10.

D—BOTANY

B. M. DUGGAR

A comparison of the absorption of inorganic elements, and of the buffer systems of legumes and non-legumes and its bearing upon existing theories. J. D. NEWTON. *Soil Science* 15, 181-204 (1923).—Comparisons at 4 different stages of growth of percentage compn. and of ratios in which ion equivs. were absorbed show no characteristic differences with barley and peas or barley and vetch. Beans absorb more Ca in proportion to K from a given nutrient soln. than either barley or peas. The quantity of Ca absorbed did not depend upon the amt. of N absorbed. The amt. of Ca absorbed was decreased by growing the plants in solns. low in Ca; in this case the amt. of N absorbed was not changed. Inoculated peas absorbed more N than uninoculated ones but the amt. of Ca taken up was the same. When grown side by side in an adobe soil peas contained more Ca than barley. The quantity of CO₂ evolved by the roots of peas was much higher than with barley. The larger amt. of CO₂ was probably responsible for the larger amt. of Ca rendered available. The *pH* value of the sap of peas, beans, and barley was not appreciably increased by limiting the supply of Ca. As a whole the results do not confirm the Truog theory as to the function of Ca in plants.

R. BRADFELD

The influence of neutral salts on the ultramaximum temperature of *Tradescantia zebrina*. HUGO KAHN. *Acta et Comm. Univ. Dorpat.* 2A, 1-42 (1921); *Chem. Zentr.* 1922, III, 926.—Alkali salts enhance the heat coagulation of the plasma according to the following lyotropic series: KCNS, KBr, KI, KNO₃, KCl, MeCO₂K, K tartrate, K citrate, K₂SO₄, NH₄CNS, NH₄I, NH₄Br, NH₄NO₃, NH₄Cl, (NH₄)₂SO₄, NaCNS, NaBr, NaI, NaNO₃, NaCl, MeCO₂Na, Na₂SO₄. The difference in the action of alkali cations is less pronounced than that of the anions. In SrCl₂, BaCl₂ and MgCl₂ solns. the coagulation temp. of the plasma is higher than in alkali chlorides, with an intermediate value for CaCl₂. The enhancing action of the cations is in the order: K > NH₄ > Na, Li, Ca > Sr, Ba > Mg. The coagulation temp. is higher in alk. than in neutral soln. The OH ions equalize in general the differences between the effect of the anions of the neutral salts, and the differences in temp. between the individual members of the lyotropic series are smaller than in neutral solns. For K salts (0.8 N salt + 0.001 N NaOH) the temp. differences are KCNS, + 4.7°; KI, + 3.2°; KNO₃, + 2.4°; KCl, + 0.5°; MeCO₂K, + 1.5°. With salts therefore which in neutral soln. lower the coagulation temp. most, like thiocyanates and iodides, the temp. is increased the most relatively in the presence of OH ions. In acid solns. (0.001 N (CO₂H)₂) the temp. is in general lower than in neutral solns. The influence on coagulation of acids is greatest for the most active members of the lyotropic series (CNS, I, Br). H ions, in distinction to OH ions, cause more pronounced differences in activity of the anions of the salts. The lyotropic effects, which appear in the action of neutral salts, are to be traced back to the permeability of the plant plasma, the most permeating salts lowering the temp. the most. To the higher concns. of neutral salts correspond a lower coagulation temp. of the plasma. The temp. lowering varies with the activity of the salts, and the most active salts cause a lowering of the temp. with increase in concn. relatively greater than with the tartrates, citrates, and sulfates.

C. C. DAVIS

The effect of Uspulun, formalin, copper sulfate, calcium sulfide liquor and Klorol

on the capacity for germination of sugar beet seeds. ALEXANDER CSETR. *Mitt. landw. Versuchsanst., Ungarn* 24(1921); *Chem. Zentr.* 1922, 111, 945.—Uspulun, CaSO_4 , Klorol, formalin and CaS liquor increase the energy and capacity for germination of sugar beet seeds. This increase is greatest for Uspulun and decreases in the order written above. The energy and capacity of germination were least with untreated seeds. These plant protective agents are important not only because of their fungicidal action but also for their ability to increase germination. C. C. DAVIS

The effect of potassium on the internal structure of the potato plant. VON BREHMER. *Ernahrung Pflanze* 18, 82-4; *Chem. Zentr.* 1922, 111, 628-9.—Microchem.-anatomical investigations in connection with expts. in cultivation showed that some definite cell complexes especially the parts of the plant rich in protein contained K, others none. The results show that (1) a definite amt. of K in the plant maintains the protoplasm in such condition that optimum growth takes place; (2) with too little K the consistency of the protoplasm is unfavorable to growth; and (3) with too much K the protein is salted out and a condition unfavorable to growth results. The amt. of K corresponding to optimum growth was 1520 kg. of kainite per hectare (2.5 times the amt. usually used for fertilizing). C. C. DAVIS

Chemical prophylaxis and therapy in viticulture. KARL MÜLLER. *Z. angew. Chem.* 36, 397-9(1923).—The needs of the pathologist for more efficient and cheaper fungicides and insecticides to combat parasites and prevent disease are discussed. C. N. FREY

Action of cations of salts on the decomposition and the formation of starch in plants. W. S. ILJIN. *Biochem. Z.* 132, 494-510(1922).—(A). Influence of salts on the decomposition of starch. Univalent metals stimulate the formation of optically active substances in the cells. (B). Influence of salts on the synthesis of starch. Not only the concn. of the cation but also its sp. properties influence the synthesis. The synthesis is retarded to the greatest extent by Ba, followed, in descending order, by Li, Na, K, Rb, Ca and Mg. JOSEPH S. HETBURN

Greasewood as a poisonous plant. C. D. MARSH, A. B. CLAWSON AND J. F. COUCH. U. S. Dept. Agr., *Circ.* 279, 1-4(1923).—The poisonous properties of greasewood are due to Na and K oxalates in the plant. Poisoning occurs only when a considerable quantity of the plant, at least 1.5 lbs. to the hundred wt. of animal, is eaten in a very short time, and injurious effects may therefore be avoided if animals are not allowed to graze on greasewood when they are very hungry. W. H. ROSS

Conditions for the biological action of Röntgen rays. III. EUGEN PRITYV. *Biochem. Z.* 135, 353-83(1923); cf. *C. A.* 16, 1971.—A large no. of oxidizing agents did not alter the effect of Röntgen rays on the development of seedlings, possibly owing to lack of absorption by the plant tissue. Previous treatment with H_2O_2 increased the sensitivity to irradiation; exposure to an atm. of CO_2 had the opposite effect. These effects are in no way related to the optical character of the solns., since H_2O_2 and KCN solns., similarly effective, are both optically inert. Thus previous conclusions (*C. A.* 15, 3302) are supported. GEORGE ERIC SIMPSON

The mobilization of the ash constituents and of nitrogen from wood and bark during spring exfoliation. AUGUST RIPPEL. *Biochem. Z.* 135, 518-31(1923); cf. *C. A.* 15, 1554.—Previous results on *Salix* are confirmed for *Sambucus nigra*. The principal inorg. constituents of bark and wood are detd. before and after exfoliation. In general, partition is not altered. K is an exception. It is increased in the wood. Of the mineral anions, PO_4 alone is transported. The migrating cations were originally combined as (a) inorg. PO_4 , (b) org. PO_4 (Phytin?), (c) org. acid, in which form transportation in large part occurs, (d) possibly in some other unidentified form. Inorg. PO_4 is regenerated from org. PO_4 as it is removed. GEORGE ERIC SIMPSON

The urea content of the fungi. N. N. IVANOV. *Biochem. Z.* 136, 1-8(1923); cf. *C. A.* 17, 2441.—The urea content of various fungi varies from 0.5 to 11%. It is lacking in the immature fungus. Urea is at a max. at the commencement of the ripening process, and vanishes at its completion. GEORGE ERIC SIMPSON

The formation of urea in fungi. N. N. IVANOV. *Biochem. Z.* 136, 9-19(1923); cf. preceding abstr.—The fungi are able to form considerable amts. of urea from gaseous NH_3 or NH_4 salts during ripening. GEORGE ERIC SIMPSON

The formation of citric acid from sugar in cultures of *Aspergillus niger* and *Penicillium glaucum*. V. BUTKOVICH. *Biochem. Z.* 136, 224-37(1923); cf. *C. A.* 16, 3931.—Cultures of *Aspergillus niger* in synthetic media contg. CaCO_3 , relatively little N, and much sugar, produce as much citric acid as *Citromyces glaber*. Much oxalic acid is produced by the former, traces only by the latter. An unidentified org. acid with a sol. Ca salt is also produced by both. An excessive supply of N as well as N

deficiency promotes citric acid formation. When CaCO_3 is lacking, much free citric acid, but no oxalic acid, is produced. Since the quantity of the unidentified acid decreases after a time while the amt. of citric and oxalic acid continues to increase, it is probably a precursor of these acids. *Penicillium glaucum* forms citric acid in the presence of CaCO_3 , but in small amts. only, probably because it is better able to oxidize the org. acids completely. The sepn. of the fungi into 2 groups, oxalic acid formers and citric acid formers, has no foundation and should be discarded. G. E. S.

The chemical composition of green plants. XXVI. Critique on the occurrence of tartaric acid in plants. HARTWIG FRANZEN AND FRITZ HELWERT. *Biochem. Z.* 136, 291-305(1923); cf. *C. A.* 17, 2905.—Tartaric acid is probably present in the wood of *Quercus pedunculata*. It is certainly present in the fruit of *Vitis vinifera*, *Tamarindus indica*, and *Pirus Aucuparia*, also in *Beta vulgaris* (unripe) and *Acer saccharinum* (sap). Its reported presence in other plants is based on insufficient evidence. XXVII. **The occurrence of succinic acid in plants.** HARTWIG FRANZEN AND RUDOLF OSTERTAG. *Ibid.* 327-35.—A list of 13 plants is given. GEORGE ERIC SIMPSON

The taking up of electrolytes by plants. I. The absorption of inorganic salts by means of the roots. SILVESTR PRÁT. *Biochem. Z.* 136, 366-76(1923).—During the growth of plants under const. conditions the absorption of ions proceeds steadily. It is, in general, independent of transpiration, although it is hastened by increasing transpiration. The amt. of ion absorption is directly proportional to the speed of growth (of the leaves especially); it is practically independent of the amt. of absorbing surface (root) exposed to the nutritive soln. Speed of growth, amt. of transpiration and of ion absorption are proportional to the concn. of the nutritive fluid. When CaCl_2 (0.005 M) is used as the nutritive fluid, ion absorption does not keep pace with transpiration; when KCl (0.010 M) is used, ion absorption is swifter than transpiration. *Zea mais*, *Pisum sativum*, and *Pharbitis hispida* were grown in Knop's soln. Ion absorption was measured by the decrease in cond. of the nutritive soln. C. E. S.

Constituents of the peach leaves. T. KARYONE AND Y. KIMURA. *J. Pharm. Soc. Japan* No. 494, 247-51(1923).—Japanese peach, *Pirus sinensis* Lindl. is popularly used as a respiratory sedative, and is botanically different from the European peach, *Pirus communis* L., the leaves of which are used in diarrhea, and are known to contain arbutin; Bourquelot's method is used. Japanese peach leaves were analyzed and the results compared with those obtained from European peach leaves cultivated in Kanagawa Exptl. Station. The results are given, resp., for Japanese peach leaves collected in July; the same collected in Sept. and European species: arbutin (% of dry leaves) 0.300, 0.130, 0.577%; tannin (by Schröder's method) 2.405, 2.910, 8.140%; H_2O 57.856, 49.792, 58.260; ash 7.996, 2.960, and 2.212%. S. T.

The change in quantity of sugar and tannin in the fruits of *Diospyros kaki* on loss of astringency with a preliminary report on a theory of loss of astringency. Y. KUMAGAI AND K. TAZAKI. *J. Sci. Agr. Soc. (Japan)* No. 236, 347-62(1922).—Analytical data show that tannin content does not change in *Diospyros kaki*, after loss of astringency, which supports Lloyd's contention that loss of astringency is not due to loss of tannin by decompn. but due to its change to an insol. compd. by combining with colloidal substances. The facts reported are: Kaki contains only reduced sugar (d-rotatory), and no saccharose. Kaki which has lost its astringency contains slightly less sugar than that which is untreated, and has 1-2% (fresh fruit) when its astringency has been removed by CO_2 (2 atm. pressure for 3 days). The sugar does not exist as a glucoside of tannin. Tannin contents are the same before and after the loss of astringency; the process for this, however, converts tannin to an insol. compd. The majority of insol. tannin will dissolve in H_2O when boiled for a long time, and is slightly sol. in dil. HCl or AcOH, but is insol. in EtOH; the latter, however, makes the insol. tannin more sol. in hot H_2O . Alkali (1%) dissolves tannin. All the solvents of tannin seem to dissolve protein too. The process for removing the astringency so raises the viscosity of the fruit that desiccation is difficult. A brief theory is given. S. T.

Nutrition of plants considered as an electrical phenomenon (BRAZEALE) 15. Chemical data on *Rapanea leuvenensis* (DUCLOUX, AWSCHALOM) 17.

E—NUTRITION

PHILIP B. HAWK

NORMAL

Effect of milk and its constituents on growth. I. E. STRANSKY. *Jahrb. Kinderheilk.* 49, 229-43(1922); *Physiol. Abstracts* 8, 23-4.—With 5 cc. of cow milk (without

other vitamins) rats grow normally. The effective substance of the milk is the curd (fat + casein). With vitamin A alone without native casein young rats do not grow. Animals which are fed on white bread and butter or with cod-liver oil with or without whey do not prosper. The existence of a 4th vitamin (D), which seems to be bound to different proteins, is postulated. H. G.

The respiratory metabolism of dogs after intravenous milk injections. J. SÄNGER. *Z. Biol.* 76, 301-14(1922); *Physiol. Abstracts* 8, 28.—After intravenous milk injections the temp. mounts 1 to 1.5°. There is also a considerable increase of the respiratory gaseous exchange, and the entire heat production is increased. After 4 to 8 hrs. the normal state is reached again. After thyroidectomy, the course of the temp. after milk injections is the same, but there is no increase in gaseous exchange and heat formation. H. G.

Checking of growth and development of rats fed on a vitamin-free diet. E. WOERNCK-BAUS. *Z. ges. expil. Med.* 29, 288-309(1922); *Physiol. Abstracts* 8, 23. Growing white rats fed with dog biscuit extd. thoroughly with alc. cannot live longer than 4 weeks. By adding orypan (a water-sol. vitamin B) and the ext. obtained during the manuf. of the biscuit (a fat-sol. vitamin A) the duration of the life can be extended to 11 weeks. H. G.

A proof of the regulatory influence of cod-liver oil on calcium and phosphorus metabolism. E. A. PARK, RUTH A. GUY AND G. F. POWERS. *Am. J. Diseases Children* 26, 103-111(1923).—Five expts. (16 rats in each) were carried out with a basal ration low in Ca, P and fat-sol A and desired variations in Ca and P were obtained by adding CaCO_3 and Na_2HPO_4 to this basal diet. After 35 days on the chosen ration, one-half the animals were bled and the Ca and the inorg. P of the blood serum were detd. The remaining rats were kept on the same ration as before but with the addn. to it of 2% of cod-liver oil. After ten days these animals were bled and similar detns. made. Deficiency in radiant energy and the org. factor contained in cod-liver oil causes disproportions in the concns. of Ca and P in the blood serum corresponding to such disproportions in the diet. Cod-liver oil, contg. no Ca or P, administered to an animal whose blood is deficient in Ca or P, causes the Ca or P or both to approach their normal levels. Cod-liver oil not only acts as a regulator to the Ca or P metabolism but also permits the organism to operate with greatly increased economy. The parallel effects of cod-liver oil and radiant energy on the Ca and P metabolism of the body and the existence of a latent period in both before the effects become manifest are evidence that the cod-liver oil acts on the body as a whole. I. NEWTON KUGELMASS

The effect of adding orange juice to the diets of under-weight children. FRANCES NEWELL AND ELIZABETH W. MILLER. *J. Home Econ.* 15, 241-8(1923).—An investigation of 14 school children from 5 to 13 years old showed an unmistakable rise in the wt. curve of such children produced by the daily administration of 45 cc. of orange juice. This is attributed either to the effect of added vitamin A, B, or C, or of inorg. constituents which may either supplement a deficiency of these substances or produce some other change such as a shift in the acid-base equil. L. D. ELLIOTT

Intermediary metabolism of carbohydrates. P. A. SHAFER. *Physiol. Rev.* 3, 394-437(1923).—A comprehensive review with extensive bibliography. According to the view now prevalent lactic acid represents the main intermediate in glucose metabolism. There is no obstacle to the belief that glyceric aldehyde, dihydroxyacetone and methylglyoxal (together with the hexose phosphate, "lactacidogen") represent the main intermediates between glycogen or glucose and lactic acid. The reaction $\text{glucose} \rightleftharpoons \text{lactic acid}$ is reversible, but the preponderating reaction in the presence of O_2 is $\text{lactic acid} \rightarrow \text{glucose}$. It is difficult to believe that glucose is oxidized by way of lactic and pyruvic acids and CH_3CHO . It is not unlikely that it is oxidized to a single mol. of ketolytic substance without previous splitting to triose. E. R. LONG

The basal metabolism of girls from eleven to fourteen years of age. MARY S. ROSE AND GRACE MACLEOD. *Proc. Am. Physiol. Soc., Am. J. Physiol.* 63, 399-400 (1923).—Calories per sq. m. body surface for 11 year olds (4 subjects) were 35.9 to 42.5, for 12 year olds (16 subjects) 31.3 to 51.6, for 13 year olds (10 subjects) 35.9 to 49.1, for 14 year olds (5 subjects) 31.8 to 41.4. J. F. LYMAN

The cause of the increase in basal metabolism during the initial days of fasting. MARGARET M. KUNDE. *Proc. Am. Physiol. Soc., Am. J. Physiol.* 63, 401-3(1923).—Since the increase in basal metabolism normally occurring during the initial days of fasting can be prevented by the ingestion of non-irritating, non-nutritious substances (Cellu Four wafers, consisting of cellulose, saccharin, india gum and mineral oil), the increased metabolism is probably due to afferent impulses from the empty and hypertonic gut, reflexly increasing muscle tone, rather than to chem. changes in the compn.

of the blood (acidosis) due to abnormal conditions of metabolism caused by fasting.

J. F. LYMAN

The effect of formaldehyde upon the vitamin content of milk. A. M. BLILE AND R. J. SEYMOUR. *Proc. Am. Physiol. Soc., Am. J. Physiol.* 63, 421(1923).—To test the effect of CH_2O on the vitamins of milk 2 lots of chicks were fed vitamin-free food to which raw winter milk was added to make a barely moistened mash. The milk fed to one half the chicks contained enough CH_2O to prevent souring at room temp. for 48 hrs. (1 to 20000.) The growth curves of the 2 lots were almost identical, such differences as occurred being in favor of the chicks receiving CH_2O . Xerophthalmia and polyneuritis appeared in each group toward the end of the tests, but in each case appeared in the control chicks at an earlier period.

J. F. LYMAN

Thermal regulation and muscular work of man in their relation to basal metabolism. HENRI MAGNE. *Bull. soc. hyg. aliment.* 11, 393-401(1923).—Polemical against J. Lefèvre (*C. A.* 17, 1496). J. LEFÈVRE. *Ibid* 413-6.—Answer to Magne. A. P.-C.

Basal metabolism and the critical zone of thermoregulation. J. LEFÈVRE. *Bull. soc. hyg. aliment.* 11, 402-12(1923).—A detailed discussion of L.'s reasons for recommending the immersion of the subject in a bath at 36° in detg. basal metabolism (*C. A.* 17, 1496), showing more particularly why air is not suitable. MARCEL LABBÉ. *Ibid* 417-8.—Criticisms of Lefèvre's article. J. LEFÈVRE. *Ibid* 418-22.—Reply to Labbé.

A. PAPINEAU-COUTURE

Phosphorus metabolism of the nervous system. I. ELISABETH HECKER AND HANS WINTERSTEIN. *Z. physiol. Chem.* 128, 302-16(1923).—In frogs the fresh brain and cord contain 0.20% P. The P content of the brain is about 0.5 that of the cord and the upper half of the cord contains less P than the lower half.

R. L. STEHLE

ABNORMAL

The acid-base ratio of the diet in rickets production. T. F. ZUCKER, WM. C. JOHNSON AND M. BARNETT. *Proc. Soc. Exptl. Biol. Med.* 20, 20-2(1922).—Rickets did not develop in rats fed a rickets producing diet when the food acidity was increased by giving CaCl_2 in place of Ca lactate; the addn. of 2% NH_4Cl had the same effect. A non-rachitic diet produced rickets after the addn. of 2% Na_2CO_3 . Decreased intestinal acidity may account for rickets in infants whose diet is apparently correct.

C. V. B.

Beriberi in the garrison at San Juan, Porto Rico. B. K. ASHFORD. *Am. J. Trop. Med.* 2, 305-40(1922); *Exptl. Sta. Record* 48, 262.—The pathological condition was a form of beriberi complicated by glandular deficiency induced by protein deficiency in the food. While the ration as served furnished a sufficiency of antineuritic vitamin, it contained too high a proportion of rice and fat and too little fresh meat and vegetables. Moreover, the natural food habits of the native soldiers led them to eat inordinate quantities of the polished rice, which made up the bulk of the carbohydrate of the ration. It is suggested that the supply of vegetables be increased.

H. G.

The vitamin hypothesis and its practical significance in stock feeding. J. B. ORR. *Highland Agr. Soc. Scot. Trans.* [5] 34, 52-67(1922); *Exptl. Sta. Record* 48, 368.—This is a discussion of the effects of a lack of vitamins on growth, with special regard to the doubtful applicability of the results obtained on small animals to horses, cattle, sheep, and swine, as well as a review of the vitamin studies which have been made with the larger animals.

H. G.

Therapeutic value of egg yolk in rickets. A. F. HESS. *J. Am. Med. Assoc.* 81, 15-7(1923).—Expts. with rats, and feeding tests with 62 infants led to the following conclusions: Egg yolk possesses marked antirachitic properties for animals and for infants. It has proved itself of value in protecting infants from rickets during the season when the incidence is greatest, and, can be recommended as a supplement to the dietary comparable to orange juice in the protection against infantile scurvy. It has also curative value but less than cod-liver oil, and should not be relied on for cure except when the oil is not well borne.

L. W. RIGGS

F—PHYSIOLOGY

ANDREW HUNTER

Properties and methods of preparation of the anti-diabetic substance (glucopyrron) generated by the pancreas. J. R. MURLIN. *Proc. Soc. Exptl. Biol. Med.* 20, 70(1922).—The substance is prepd. by (1) destruction of trypsin; (2) pptn. of proteins; (3) concn.; and (4) purification. Potent and non-toxic aq. exts. can be prepd. The active substance is not entirely pptd. by abs. alc. It is not pptd. by the ordinary protein

precipitants, nor dialyzable through vegetable parchment. It is readily absorbed.

C. V. B.

Influence of pancreatic extracts upon the carbohydrate metabolism of depancreatized dogs. C. B. F. GIBBS, H. D. CLOUGH, N. C. STONE, AND J. R. MURLIN. *Proc. Soc. Exptl. Biol. Med.* 20, 67-8(1922).—Two days following the operation the dogs were totally diabetic. They were given an increasing diet of ground beef and the exts. were administered by way of the stomach, muscles, veins, skin and peritoneal cavity. Sugar abruptly decreased in blood and urine and the respiratory quotients increased. Subcutaneous injections of purified alc. exts. of fresh dog pancreas proved to be the most satisfactory.

C. V. B.

Three months study of the influence of the anti-diabetic substance on a case of severe diabetes. C. C. SUTTER AND J. R. MURLIN. *Proc. Soc. Exptl. Biol. Med.* 20, 68-9(1922).—The administration of pancreatic ext. by the duodenal tube was followed by a decrease of the blood sugar and of urinary sugar and acetone. Subcutaneous injections were not irritating and caused a rapid return of the patient to normal, permitting, under daily treatment, a diet of 2500 cal. No beneficial effects followed the administration by mouth or in salol-coated capsules.

C. V. B.

Influence of pancreatic perfusates upon the carbohydrate metabolism of depancreatized animals. H. D. CLOUGH, A. M. STOKES, C. B. F. GIBBS, N. C. STONE AND J. R. MURLIN. *Proc. Soc. Exptl. Biol. Med.* 20, 66-7(1922). The pancreases of cats, dogs, pigs and oxen were perfused with Locke soln.; the animals were in a respiration chamber ventilating into a large gasometer from which samples were analyzed in a modified Haldane apparatus. D:N ratios and respiratory quotients typical for diabetes were obtained. The animals were given dextrose or sucrose and subcutaneous, intravenous or intraperitoneal injections of the perfusates; the respiratory quotients increased; blood sugar greatly decreased; and the D:N ration was markedly changed.

C. V. B.

Iron content of the blood of thyroidectomized animals. M. PARHON. *Endocrin. patol. costit.* 1, 39(1922); *Physiol. Abstracts* 8, 184-5.—In 6-weeks old sheep, after removal of the thyroid, the iron content of fresh blood fell to 0.053% from a normal figure of 0.065%, of dried blood to 0.273% from 0.328%. A relation is suggested between this and the lowered oxidations of the body.

H. G.

Hydrogen-ion concentration of saliva. V. ANDRESEN. *Ergeb. ges. Zahnheilk.* 6, 59-85(1922); E. POHLE AND E. STREIBINGER. *Deut. Monatsschr. Zahnheilk.* 40, 306-9(1922); *Physiol. Abstracts* 8, 13-4.—In the first of these papers it is shown that the mucous and serous parts of the saliva possess a different C_{H} , and that the greater proportion of the buffer substances is to be found in the serous part. The saliva as a whole gives an amphoteric reaction. Work on the connection between caries and salivary reaction is critically considered. Finally, the mineral content of the saliva is dealt with from the point of view of therapeutic and prophylactic value of Ca phosphate and carbonate solns. The second paper is concerned with the reaction of the saliva as a causative factor in caries. The authors find that in healthy people with normal teeth all gradations are possible between markedly acid and alk. saliva. The individual diurnal variations are also given. Variations in sp. gr. accompany those in reaction. They find that buffering in the saliva is very slight, and correlate this with its poverty in salts.

H. G.

Further observations on the thymus gland. J. LEHRER. *Vlaamsch geneesk. tijds.* 21, 489-95(1921); *Physiol. Abstracts* 8, 66.—A review. L. thinks that the thymus is not to be regarded as an internally secreting gland, but as an organ with a biochem. role—namely, the regulation of the metabolism of the org. P compds. of the body, the nuclein substances.

H. G.

Physiological occurrence of iron in the central nervous system. M. MÜLLER. *Z. ges. neur. Psychiat.* 77, 519-35(1922). Detection of iron in the brain especially in the center of the extrapyramidal-motor systems. I. H. SPATZ. *Ibid* 261 399; *Physiol. Abstracts* 8, 60-1.—The conclusions of these two authors are similar in many respects. The iron of the brain may be 'formed' or diffuse. The formed iron is found in glia and nerve cells, and gives a particularly intense reaction in the globus pallidus and substantia nigra. Müller finds the diffuse divided iron mainly in vessel walls and myelinated nerve fibers. Spatz finds an increase of brain iron in some cases of extrapyramidal paralysis, and iron-contg. pigment in the perivascular infiltrations characteristic of progressive paralysis and sleeping sickness. The normal, regularly occurring iron of the brain bears no relationship to the destruction or formation of hemoglobin.

H. G.

The respiratory rate in nervous tissue. A. R. MOORE. *Proc. Path. Soc. Phila-*

delphia 23, 24-5(1921); *Physiol. Abstracts* 8, 59.—The extent of the production of CO_2 in nerves was estd. colorimetrically by means of phenolsulfonephthalein, by detg. the time in which the fluid in which the nerve was kept attained a standard color. The sciatic nerve of the frog appears by this method to give a CO_2 production equal to 10-20% of that of the medulla oblongata, and about 30% of that of muscle. Elec. stimulation does not raise the value, whence it is concluded that excitation and conduction processes in nervous tissue do not depend upon the oxidation of C to CO_2 . H. G.

Fractional elimination of urea and ammonia in fatigue. A. AZZI. *Arch. sci. biol.* 4, 106-22(1923); *Physiol. Abstracts* 8, 51.—Investigations were carried out in an untrained subject on high mountains. During fatigue the elimination of urea and NH_3 was smaller, but the total acidity of urine greater than when the same subject was resting. H. G.

Measurement of blood pressure during sleep. C. MÜLLER. *Acta Med. Scand.* 55, 381-485(1921); P. BLUME. *Ugesk. Læger.* 84, 1126-32(1922); *Physiol. Abstracts* 8, 35.—The blood pressure is remarkably const. during sleep, in spite of variations when awake (men 94, women 88, children aged 3-14, 64-80 mm. Hg). Blume confirms this; the only exception is in glomerular nephritis, where the pressure is higher. He induced sleep by doses of veronal stated to have no effect on blood pressure. H. G.

Some correlations between the parathyroid functions and the enteric juice. C. ARTOM. *Arch. fisiol.* 20, 369-404(1922); *Physiol. Abstracts* 8, 185.—After total thyro-parathyroidectomy the secretion and digestive activity of the enteric juice are considerably diminished. Invertin is reduced to 19.9% and erepsin to 41.7% of the normal values. These changes are due to the removal of the parathyroids because they are not seen after simple thyroidectomy, and are observed even after partial destruction of the parathyroids alone. In this last case the diminution in the digestive activity of the enteric juice is even more remarkable than after total thyro-parathyroidectomy, because animals deprived of thyroid and parathyroids die before the symptomatology of parathyroid deficiency is fully developed. The changes due to partial parathyroidectomy disappear after a time. The administration of sol. salts of Ca to animals deprived of the thyroid and parathyroids accentuates the symptoms of parathyroid deficiency. H. G.

Metabolism by heat regulation. R. PLAUR. *Z. Biol.* 76, 183-212(1922); *Physiol. Abstracts* 8, 28.—When the external temp. is high the O usage of the body is reduced (see *Z. Biol.* 74, 191(1922)). The site of the reduction is now sought. For external temps. between 10° and 30° the heat production in the liver is controlled by nervous impulses. Dogs and cats rendered poikilothermic by artificial means were studied. The O_2 usage showed little change with body temp. over the range of normal body temps., whereas below and above these limits the curve shows the steep slope which would accord with van't Hoff's rule. The curve reaches a max. at 41.5° . The heat produced in the liver falls off as the temp. rises. This regulation is lost on destruction of the hepatic plexus. The relations of muscular tonus and shivering are also discussed. H. G.

The respiratory exchange, blood reaction, and level of phosphoric acid in the blood during mental work. H. W. KNIPPING. *Z. Biol.* 77, 165-74(1922).—Mental work is accompanied by only small increases in heat production. Nevertheless, on the commencement of such work, there is an immediate rise in the respiratory quotient which then rapidly decreases to a value below that found at rest. From analyses of the H_2PO_4 content of the blood before and during mental activity, it is concluded that this effect is due to the entrance of free H_2PO_4 acid into the blood with the consequent liberation of CO_2 . J. C. S.

Observations on the effect of high altitude on the physiological processes of the human body, carried out in the Peruvian Andes. JOSEPH BARCROFT. *Trans. Roy. Soc. London* 211B, 351-480(1923).—The chief result obtained by the expedition is that the lungs do not secrete O. The pressure of O in the blood was so nearly the same as that in the alveolar air that the passage of the gas through the pulmonary epithelium can only be attributed to diffusion. The increased concn. of corpuscles at high altitudes is not merely to transport a certain quantity of O; it also brings about an extra degree of buffering of the blood, allowing of a more alk. corpuscle at a given CO_2 pressure of 25 mm., a higher dissoc. curve, and therefore a corpuscle which is more acquisitive of O in the lung. J. C. S.

The internal secretions of the reproductive organs. F. H. A. MARSHALL. *Physiol. Rev.* 3, 335-58(1922).—A review with bibliography. The question as to the supposed rejuvenating influence of hypertrophy of the interstitial gland is still an open one, but there is no doubt that in mammals the secretion elaborated by this organ is responsible

for the development of the pubertal characters, while there is accumulating evidence that the predecessor to this gland in fetal life is a very important factor in sexual differentiation before birth. E. R. LONG

The interrelationship of blood fat and blood sugar. T. H. OLIVER AND A. HAWORTH. *Lancet* 1923, II, 114-6.—Blood sugar has a relation to blood fat other than that of a mere oxidizing agent. Fat properly absorbed into tissues increases the storage of carbohydrate; if not so absorbed, or if mobilized by Ca, storage is interfered with. Such improper storage may account for the tendency of a high fat diet to produce *glucosuria* in some cases of *diabetes*. Practically all conditions leading to hyperglucemia lead to lipemia. Adrenaline injection increases the sugar, and the fat from 0.48 to 0.56%. Both are probably stored and liberated together. E. R. LONG

Insulin. J. J. R. MACLEOD. *Lancet* 1923, II, 198-204.—A review. E. R. L.
The distribution of vitamin A in the urine and the digestive secretions (man, dog). ETHEL COOPER. *Proc. Am. Physiol. Soc., Am. J. Physiol.* 63, 425(1923).—Various body fluids (urine, saliva, gastric juice, pancreatic juice and bile) were tested by evap. to dryness and extg. with EtOH and Et₂O, the exts. being added to a standard rat diet, adequate for growth and maintenance, except for vitamin A. In general the fluids tested contain little or no vitamin A when collected from subjects on ordinary mixed diets. When the food is richer in vitamin A (e. g., cod-liver oil, eggs and milk included) the vitamin could be demonstrated in most of the secretions tested, including the urine. The exts. of bile were highly toxic, therefore no indication as to vitamin content could be obtained. J. F. LYMAN

The mechanism of the action of insulin. N. A. McCORMICK, J. J. R. MACLEOD, K. O'BRIEN AND E. C. NOBLE. *Proc. Am. Physiol. Soc., Am. J. Physiol.* 63, 389 (1923).—Since insulin administered to rabbits, irrespective of nutritive condition of the animals and of dosage, causes approx. the same abs. fall in blood sugar, and since this fall is not due to increased intravascular glucolysis, nor to polymerization of dextrose in the blood, it is argued that the insulin must enter the tissue cells and create therein a vacuum for dextrose as a result of which sugar is withdrawn from the blood more quickly than the liver and muscles can supply it from their stores of glycogen. This vacuum for dextrose is due (1) to polymerization of dextrose, (2) to increased oxidation, and (3) to reduction of dextrose with the formation of fat. J. F. L.

Delayed manifestation of the physiological effects of insulin following the administration of certain pancreatic extracts. J. B. COLLIP. *Proc. Am. Physiol. Soc., Am. J. Physiol.* 63, 391-2(1923).—Several cases have been noted where certain exts. of pancreas failed to produce the characteristic insulin hypoglycemia in normal rabbits; but did cause a low blood sugar in from 1 to 4 days following the treatment. From this it is argued that the islet cells do not contain an active insulin but rather an inert mother substance. Certain methods of extn. yield an active insulin, while other methods yield the inactive substance which becomes activated after it is injected into the animal. J. F. LYMAN

Effect of stimulation of the sensory nerves upon the rate of liberation of epinephrine from the suprarenal glands. SAKUJI KODAMA. *Tohoku J. Exptl. Med.* 4, 166-242 (1923).—The "cava pocket" method of Stewart and Rogoff was applied to cats, dogs and rabbits. Explicit directions are given for performing the expts. and the results are shown in 9 tables and 29 cardiographs. *Summary:* A distinct increase of the rate of epinephrine output from the suprarenal glands by sensory stimulation was detected. The increase was caused either solely by the increase of the epinephrine concn. of the blood from the suprarenal veins, or by the coöperation of an increase of the blood flow through the suprarenal glands, or chiefly by the latter. In some cases no effect upon the rate of epinephrine output was observed upon sensory stimulation. The rate of epinephrine output under the unavoidable exptl. conditions of the cava pocket method, as anesthesia, laparotomy, tying of blood vessels, etc., but without applying any particular manipulation such as stimulation of the nerve as a centripetal one, asphyxia, etc., does not range within so narrow a limit. As a rule, the amt. of epinephrine left in the suprarenal glands, the epinephrine output from which was largely augmented by sensory stimulation, was greater in comparison with that of the cases where the augmentation of the epinephrine output by the same manipulation was small. L. W. RIGGS

Production of epinephrine by the adrenal cortex. F. A. HARTMAN. *Science* 58, 74(1923).—The method used was to destroy the medulla of one adrenal by the electric cautery several days before the expt. The reaction to shutting off air from the lungs for 40 sec. upon a denervated pupil was measured, then the sound adrenal was removed. After recovery from the anesthetic the pupil response to shutting off air from

the lungs was again detd. The cauterized adrenal was removed and a final test of the denervated pupil was made after recovery from anesthesia. A small portion of the medulla remained in 5 of the animals. In 4 of the remaining 9 the cortex was nearly destroyed. The 5 cats with healthy cortex and no medulla in the cauterized adrenal gave good denervated pupil reactions to shutting off the air after removal of the uncauterized adrenal. After removal of the cauterized adrenal the denervated pupil gave a much smaller reaction or none. Material from the cortex gave positive tests for epinephrine by the Polin, Cannon and Denis reaction. L. W. RIGGS

Action of Vichy water on the reaction of the urine. A. DESGREZ AND H. BIERRY. *Compt. rend.* 177, 143-6(1923).—Samples of urine were collected on arising in the morning and before eating up to 8:30 or 9:30 A.M. with precautions to avoid loss of CO_2 . The p_{H} and CO_2 content were detd. immediately. The subject then drank 175 cc. of Vichy and 1 hr. later another 175 cc. Two hrs. later the p_{H} and CO_2 of the urine were detd., and an analysis of both samples was made to det. d., ash, total solids, uric acid, urea and the mineral elements. The apparent acidity A_a (phenolphthalein indicator), and the phosphatic acidity A_p , which is the acidity detd. by calcg. the phosphate to the monometallic state, were detd. The p_{H} before drinking Vichy was 5.2, and 2 hrs. after drinking Vichy, 7.2. The calcd. acidity or balance of the equivs. A_a of urine with p_{H} 5.2 was less than the apparent acidity so that $A_a - A_c = 10$. In the sample with p_{H} 7.2 on the contrary $A_c - A_a = 12$. The ratio A_a/A_p was 1.3 > 1 in the first and 0.48 < 1 in the second. Between p_{H} 5.2 and p_{H} 7.2 there exists a crit. point for which $A_a/A_p = 1$, which lies between 6.0 and 6.5. It appears that each individual possesses a urinary p_{H} which varies in different subjects from 4.6 to 7.3. Previous knowledge of this p_{H} is indispensable in detg. the threshold dose. Carbonic acid is intimately related to ionic acidity in general. Above p_{H} 6.5 the proportion of total carbonic acid increases rapidly with the p_{H} . L. W. RIGGS

The normal phosphate and sulfate content of human cerebrospinal fluid. FELIX HAUROWITZ. *Z. physiol. Chem.* 128, 290-301(1923).—The normal figures are 0.0018% P and 0.0011% S. Org. P is not present. R. L. STEHLE

G—PATHOLOGY

H. GIDEON WELLS

A study of light waves in relation to their protective action in rickets. A. F. HESS, A. M. PAPPENHEIMER AND M. WEINSTOCK. *Proc. Soc. Exptl. Biol. Med.* 20, 14-6 (1922).—White rats fed a rickets-producing diet were protected against rickets by daily irradiation for 2 min. by the Hg vapor quartz lamp at 3 ft. and a voltage of 76. By interposing standard glass filters it was detd. that rays as long as 334μ have little or no protective action; the effective rays begin in the neighborhood of 313μ . C. V. B.

Reactions of the capillary endothelium in peptone shock. W. H. MANWARING, W. H. BOYD AND W. O. FRENCH. *Proc. Soc. Exptl. Biol. Med.* 20, 52-3(1922).—Isolated canine tissues were perfused with 1% Witte peptone in Ringer soln. or blood. The liver and lungs showed a marked increase in perfusion resistance, max. in 90 sec., normal in 8 min. The intestines and hind quarters showed the opposite effect. Histologically, the liver and lungs showed marked capillary constriction with stasis, diapedesis and edema. C. V. B.

The production of acidosis by anoxemia. A. E. KOEHLER, E. H. BRUNQUIST AND A. S. LOEVENHART. *Proc. Am. Physiol. Soc., Am. J. Physiol.* 63, 404(1923).—Anoxemia was produced in pigs by exposure to an atm. low in both O_2 and CO_2 . The respiratory rate rises under these conditions from a normal of about 40 to 200 per min. In the early stages of anoxemia there is a definite increase in p_{H} of the blood (alkalosis) from 7.4 to 7.55 owing to the rapid removal of CO_2 from the blood because of the increased lung ventilation. When anoxemia is continued several hrs. the p_{H} of the blood returns to normal and continues to fall. Just before respiratory failure and death a p_{H} of 6.7 was frequently observed, with a total blood CO_2 content of only 10%. It is believed that the production of fixed acids begins at once with anoxemia but does not keep pace with the loss of CO_2 from the blood so that alkalosis is first noted. J. F. LYMAN

KORENCHESKIL, V.: **The Etiology and Pathology of Rickets from an Experimental Point of View.** London: H. M. Stationery Office. Special Rept. Series No. 71. Med. Res. Council. 172 pp. 4s. net. Reviewed in *Physiol. Abstracts* 8, 157; also in *J. Am. Med. Assoc.* 81, 683(1923).

H—PHARMACOLOGY

ALFRED N. RICHARDS

Adrenaline content of the adrenals after irradiation with X-rays. O. DAVID AND ARNOLD HIRSCH. *Klin. Wochschr.* 2, 790(1923).—The adrenaline content of the adrenals is decreased after irradiation of the adrenals with 1 erythema dose and increased after irradiation with 0.25 erythema dose.

The action of atropine on the musculus dilatator pupillae. C. F. ROCHAT AND T. P. FREESTRA. *Nederland. Tijdschr. Geneeskunde* 67, II, 406-7(1923); cf. C. A. 17, 2001.—Atropine acts in a concn. of 3:100,000 upon a sector of the iris.

Experimental basis of endocrine therapy. A. J. CLARK. *Brit. Med. J.* 1923, II, 51.—A general lecture.

Administration of insulin by inunction. S. V. TELFER. *Brit. Med. J.* 1923, I, 715-6.—Inunction of (crude) insulin mixed with lanolin or lard, on rabbit abdomens, is claimed to give the usual lowering of blood sugar.

Effects of quinine therapy on the basal metabolism in the treatment of hyperthyroidism. J. H. SPENCER AND N. V. LOTHIAN. *J. Roy. Army Med. Corps* 41, 40-7 (1923).—Quinine-HCl, 40 grains daily, reduced the B. M. R. from +25 to -14% (patient resting in bed). When allowed to get up, his B. M. R. rose to -5%. His clinical condition was improved.

The chemotherapeutic activation of preparations of arsphenamine based on experimental rabbit syphilis. W. KOLLE. *Arch. Dermat. Syphilis* 138, 97-119; *Chem. Zentr.* 1922, III, 684-5; cf. C. A. 17, 418.—Intravenous injection of sol. Hg compds. in an excess of arsphenamine is relatively harmless, since the Hg preps. oxidize the arsphenamine. It is recommended that Hg compds. of weak oxidizing power be used so that the As compds. remain intact; HgCl₂ is the least suitable and novarsol is best adapted. The effect of all arsphenamine preps. except H₂O-sol. Hg arsphenamines can be increased by admixt. with Hg compds. in so far as their action on the spirochete is concerned. The effect of the mixts. is not comparable with that of metal arsphenamines. Combination of metal arsphenamines with sol. Hg compds. leads to a further chemotherapeutic activation of the arsphenamine. The mixt. of neosilver arsphenamine with novarsol appears promising. Mixts. of neoarsphenamine and HgCl₂ according to Linser should not be used.

The treatment of skin and sexual diseases with lotions of organisms and parenteral introduction of non-specific substances. WHICHAERT. *Arch. Dermat. Syphilis* 138, 160-9; *Chem. Zentr.* 1922, III, 531-2.—Exception is taken to the careless use of the term "alterative" in connection with protein therapy. Non-sp. therapy is concerned only with an increase of functions already present. The powerful properties of the high mol. protein decompn. products are not due to these decompn. products being particularly labile. Repeated injections of various chem. compds. in small doses give the same symptoms as high mol. protein decompn. products, e. g., colloidal Pd, HCN and methylene blue. Metabolism is for short intervals after such injections so influenced that active decompn. products are formed such as are obtained from muscular exts. and other organs as non-dialyzable decompn. products. The decompn. products of lower mol. wt. play no particular part in protein therapy. An important feature of the problem is the stimulation of prophylaxis through the formation of decompn. products in the body which can inhibit the growth of agents of infection, and which are vitamin-like growth-promoting compds. which can be obtained from org. alc. exts. The exts. promote the growth of streptococci but above an optimum amt. inhibit the growth.

The secondary effects of various arsphenamine preparations especially in women. KUZNITZKY AND FUCHS. *Arch. Dermat. Syphilis* 138, 222-34; *Chem. Zentr.* 1922, III, 532.—Women are in general more endangered than men. A description is given of the appearance, after injection of arsphenamine, of icterus, severe genital discharges of blood in women, edema, rheumatic pains and angioneurotic symptoms.

Is the fever arising after the first dose of mercury and arsphenamine to be regarded as purely specific? II. GERHARD ASSMANN. *Arch. Dermat. Syphilis* 140, 235-9; *Chem. Zentr.* 1922, III, 532.—A continuation of earlier investigations on the rise in temp. after treatment with arsphenamine (cf. *Arch. Dermat. u. Syphilis* 135, 20; *Chem. Zentr.* 1921, III, 1099) dealing with neo-, Na- and Ag-arsphenamine. The greatest increase in temp. of syphilitics and non-syphilitics occurred with Ag-arsphenamine. Ag-arsphenamine caused the greatest increase in temp. and also affected

the largest no. of syphilitics and non-syphilitics whereas Na-arsphenamine caused a rise in temp. among the smallest proportion of patients. C. C. DAVIS

Mercury tolerance and elimination in syphilis therapy. GEORG GJORGJEVIC. *Arch. Dermat. Syphilis* 140, 240-6; *Chem. Zentr.* 1922, III, 568.—The cases under investigation received injections of 10% *hydrargyri salicylas* suspended in vaseline or in liquid paraffin. Men received a max. of 26 injections in 58 days, women 18 in 23 days. Women tolerated on an av. more injections than men. Where Hg did not lead to poisoning, excretion without particular effect probably occurred. Excretion of Hg through the urine was detected 3 mos. after the last injection. Forced treatment with Hg had no influence on its excretion. C. C. DAVIS

Tar melanosis (contribution to its clinical symptoms and causes, together with a few theoretical considerations of the pigment problem). A. KISSMEYER. *Arch. Dermat. u. Syphilis* 140, 357-68; *Chem. Zentr.* 1922, III, 640-1.—Based on a case of tar melanosis whose clinical symptoms and histology are described, the theory is derived that this condition arises from an excess of propigment. This pigment originates from the aromatic compds. of crude tar which are absorbed directly by the organism. A relation is sought between this tar melanosis and Addison's disease and perhaps ochrochromic conditions and the possibility is suggested that by means of the Bloch pigment theory a pathogenetic classification of pigment anomalies can be made. C. C. D.

The cellular immunity of red blood corpuscles toward pyrodine. SEBASTIANO ZISA. *Arch. patol. clin. med.* 1, 165-93; *Chem. Zentr.* 1922, III, 301.—Animals receiving preliminary treatment of pyrodine show an increased power of resistance of the blood cells toward the hemolytic effect of the poison. This is a true immunity and not an increased power of resistance of newly formed cells. The possibility of the formation of antibodies should not be overlooked. C. C. DAVIS

The blood platelets in the blood of animals poisoned by carbon monoxide and blood poisons. GIUSEPPE BIANCHINI AND S. M. FABBRONI. *Pathologica* 14, 230-4; *Chem. Zentr.* 1922, III, 940-1.—In rabbits poisoned with CO the no. of blood platelets gradually increased to twice the no. but returned to the initial no. in 2 hrs. By repeating expts. several days in succession on the same animals the increase gradually became less. The other blood elements were not affected. Inhalation of O shortened the return to normal of the platelet count. Guinea pigs in which thrombopenia had been produced by the method of Sacerdotti immediately showed symptoms of thrombocytosis again under the influence of CO. C. C. DAVIS

The blood platelets in the blood of animals poisoned with carbon dioxide. GIUSEPPE BIANCHINI AND GASTONE PAGNI. *Pathologica* 14, 235-7; *Chem. Zentr.* 1922, III, 941; cf. preceding abstr.—Thrombosis was produced in rabbits after removal of the spleen by slow poisoning with CO₂ with return to normal in 24 hrs., although to a less extent than with CO. Inhalation of O at the height of the thrombocytosis caused a rapid reduction in a few moments to the normal value. Artificially produced thrombopenia (best 5 hrs. after injection of the serum of Sacerdotti) quickly ends under treatment with CO₂ or by mech. suffocation. C. C. DAVIS

The copper therapy of tuberculosis. E. TROCELLO. *Rass. clin. terap. sci.* 21, 85-105; *Chem. Zentr.* 1922, III, 683.—From a detailed survey of the literature and independent observations it is concluded that the undoubtedly favorable effects of Cu compds. on tuberculosis cannot be explained on chemotherapeutic principles, since amts. tolerated without injury show only the slightest parasitotropism. The effect depends essentially on a special affinity for the pathological tissue. The tissue in contact with the sp. focus is irritated and rapidly forms connective tissue which isolates the bacillary and necrotic foci. The most suitable Cu compds., their doses and methods of use are yet to be detd. "Cuprocyan" and especially "Cuproiodase" give undeniably favorable results in many forms of tuberculosis. The foregoing explains the varying results in pulmonary tuberculosis. C. C. DAVIS

The chemotherapy of tuberculosis. VIRILIO FERRARI. *Rass. clin. terap. sci.* 21, 116-28; *Chem. Zentr.* 1922, III, 683.—The use of "Cuprocyan" and "Cuproiodase" are proved to be harmless. In a few cases distinct improvement in the blood took place. No influence on the temp. nor any particular improvement in the general condition was observed. C. C. DAVIS

Adsorption and its relation to pharmacology. E. KESSER. *Ber. pharm. Ges.* 33, 114-9(1923).—A discussion of certain adsorption phenomena, notably from the standpoint of positively and negatively charged ions of medicaments in acid and alk. media, with or without the action of animal charcoal. Expts. are noted involving the recovery of salicylic acid and I from different individuals. They indicate among other

things how adsorption of a given medicament may be increased or diminished, with a corresponding diminution or increase in resorption. W. O. F.

Biologic and chemical-physical experiments on some complex copper cyanides. A. CHISTONI. *Arch. sci. biol.* 4, 1-20(1923); *Physiol. Abstracts* 8, 86. Expts. were made with 3 different cyanides of Cu and K. The subcutaneous injection of diluted water solns. of these cyanides did not give rise to any special local reaction, but to general toxic lesions chiefly of the kidney; these were the more severe the greater was the content in Cu in the solns. used. This toxic effect is probably due to a complex anion, Cu(CN). H. G.

Action of pine pollen on the heart of some animals. C. FEDERL. *Atti. accad. Lincei, Rend.* 31, 390-1(1922); *Physiol. Abstracts* 8, 34. Dil. solns. of the ext. obtained from pine pollen diminish the heart's activity, an effect from which recovery can be made. Conc'd. solns. produce a diastolic ventricular standstill from which a greater or lesser contracture develops, the auricles beating feebly. Frequently phases of diastolic standstill alternate with normal heart beat. H. G.

Hypersensitiveness. W. S. V. LEEUWEN. *Brit. Assoc. Rept. Hull* 1922, 391; *Physiol. Abstracts* 8, 85; cf. C. A. 17, 414-5.—The action of drugs on isolated organs in Tyrode solution is an instance of hypersensitiveness, since the drugs are not inhibited by blood constituents. Drug action can be augmented by substances which do not stimulate *per se*; examples are given. Hypersensitiveness is due to lack of fixing power of the blood for the drug. H. G.

Passage of ingested alcohol into the principal tissues and organs. S. A. KOSTITCH. *Intern. Z. Alkoholismus* 30, 153-67(1922); *Physiol. Abstracts* 8, 192. EtOH after absorption is distributed in all organs and there remains, bringing on gradually all the changes found in alcoholism, until it is rendered innocuous by combustion. It is not attacked by the digestive juices, but influences their secretion, producing, e.g., a hypersecretion of salt. Of small doses about 5% is excreted by the kidneys, skin, and lungs. K. has investigated the affinity of the various organs, particularly the germinal glands, for EtOH, working on pigs and guinea pigs. The EtOH can be found in liver, brain, kidney, muscles, suprarenals, blood, and bile. In a pregnant sow the content of maternal and fetal blood was nearly identical. EtOH was found both in the amniotic fluid and fetal organs. In the testes the EtOH content is the same as that in the blood; in the ovaries it is increased. H. G.

Protein therapy and blood coagulation. R. SALOMON AND W. OPPENHEIMER. *Monatsschr. Geburtshilfe Gynäkologie* 9, 124-35(1922); *Physiol. Abstracts* 8, 40.—Acceleration of coagulability is effected by protein therapy. H. G.

Alkali therapy. The effects of administration of measured quantities of sodium carbonate on the carbon dioxide carrying power of the plasma. S. P. REIMANN. *Proc. Path. Soc. Philadelphia* 23, 35(1921); *Physiol. Abstracts* 8, 43. After intravenous injection of bicarbonate into dogs the quantity in the blood was calcd. The time taken to reach the max. content is somewhat in excess of that calcd. from the formula of Palmer and Van Slyke. The formula is, however, in general applicable. H. G.

Lactic acid as a cardiac and muscular poison and the antitoxic action of adrenaline, cholesterol and glucose. BLANCO SOLER. *Prog. clin. (Madrid)* 1922, 1-14; *Endocrinology* 7, 326-7.—S. has studied the neutralizing action of adrenaline and cholesterol in connection with lactic acid and ascribes antitoxic properties to the adrenals and the organs of internal secretion in general. Numerous plates illustrate the paper. H. G.

Experimental studies on the action of the extract of the posterior hypophysis on urinary secretion. M. GARNIER AND E. SCHULMANN. *Rev. neurol.* 19, 630-3(1922); *Physiol. Abstracts* 8, 184.—Subcutaneous injection of the ext. obtained from ox and horse diminishes the water output in rabbits and dogs, without damaging the coney. mechanism. Ordinary polyuria following administration of water is also diminished. The removal of lipoids from the ext. with chloroform does not affect this diuretic power, which must be due therefore to some other substance in the posterior lobe. H. G.

Effect of adrenaline on human blood pressure and blood sugar with different modes of injection. P. SCHENK AND A. HEIMANN-TROSIEN. *Z. ges. exper. Med.* 29, 401-11, 1922; *Physiol. Abstracts* 8, 64.—The cleavage of adrenaline seems to take place partly in the capillaries. The effects of subcutaneous, intravenous, and intra arterial injections of adrenaline have been compared. The dose of the intra-arterial injections can be adapted to that of subcutaneous injections, while intravenous injections can only be applied with the greatest care, slowly, and at great diln. H. G.

Action of some sodium salts and of cold upon the agglutination of foreign particles by the blood platelets. J. ROSKAM. *Compt. rend. soc. belge biol.* 1, 100-1(1922); *Physiol. Abstracts* 7, 292-3.—Cold and certain neutral Na salts in sufficient concn. mark-

edly retard, even totally prevent, the agglutination of foreign particles by the isolated washed blood platelets of the rabbit in the presence of plasma. Sensitization of the particles by the plasma is inhibited.

JOSEPH S. HEPBURN

Pigmentary effector system. II. I. T. HOGREN AND F. R. WINTON. *Proc. Roy. Soc. (London)* **94B**, 151-62(1922); cf. *C. A.* **16**, 3512.—Melanophore contraction was produced by caffeine and by the following compds. which excite peripheral sympathetic nerve endings: adrenaline, tyramine, ergotoxin, and cocaine. Melanophore expansion was produced by pituitary ext. and by apocodine and nicotine in doses sufficient to paralyze all sympathetic nerve endings. No unequivocal direct evidence has been advanced to demonstrate a nervous control of pigment responses in Amphibia. The synchronous color changes in these animals in response to normal environmental stimuli are possibly detd. mainly by endocrine influences. **III. Color response in the hypophysectomized frog.** *Ibid* **95B**, 15-31(1923).—Ext. of the posterior lobe of the pituitary gland of mammals, birds, reptiles, amphibians, and fishes exerts a sp. local action on the melanophores of the frog, producing max. expansion in the intact animal, the isolated limb, and the isolated strip of skin. The gland of a single frog yields sufficient active principle to produce darkening in more than 50 other frogs; this principle differs from the pressor and agrees with the uterine component in certain biochem. properties. Removal of the anterior lobe of the pituitary does not influence the normal sequence of pigmentary response. Removal of the entire gland produces complete contraction of the melanophores and max. expansion of the xantholeucophores. While injection of posterior lobe ext. into a hypophysectomized frog evokes the characteristic expansion of the melanophores, yet the exptl. animal regains pallor even when exposed to an environment which would cause darkening of a normal frog. Intravenous administration of sympathomimetic reagents (*e. g.*, adrenaline and tyramine) produces pallor in dark normal frogs; nicotine and apocodeine, in dosage sufficient to cause motor paralysis, give rise to a partial darkening associated with a stellate appearance of the melanophores in both normal and hypophysectomized frogs. Pilocarpine and atropine have no action on the melanophores. The color changes of the intact frog are attributed to fluctuating activity of the secreting mechanism of the posterior lobe of the pituitary in response to such natural factors as temp., light, humidity, or to the rapidity with which the melanophore stimulant of the pituitary secretion is eliminated under the influence of these factors.

JOSEPH S. HEPBURN

Novasurol diuresis and kidney function. HEINRICH SCHUR. *Wiener Arch. inn. Med.* **6**, 175-215(1923).—Clinical and exptl. study indicate that the kidney is the point of attack of novasurol, as of most other diuretics. The diuresis is independent of the salt and water content of the serum, and is the result of heightened normal kidney function in causing increased swelling of the kidney cells followed by shrinking of the cells with excretion of the diuretic agent and it is probable that not all of the secreting kidney cells function alike and that the secretion of a dil. urine poor in NaCl is differently produced from a concd. urine rich in NaCl. It is probable that there are special mechanisms for the excretion or retention of certain substances as phosphates, uric acid and glucose that are not eliminated with either H₂O or NaCl.

HARRIET F. HOLMES

Behavior of nevalteine with quinine salts: easy method for its identification. MARIO CARDINI. *Boll. chim. farm.* **60**, 253-8(1921).—The following reaction has been tested with all the antipyretics at present in use, and is found to be given only by nevalteine (Na *p*-phenetidinomethanesulfonate): A small quantity (0.02 g.) of the substance and 0.01 g. of quinine hydrochloride or sulfate are treated together in a porcelain dish with a drop of water, a characteristic reddish yellow coloration being obtained with nevalteine.

J. C. S.

Magnesium metabolism. Influence of subcutaneous injection of magnesium sulfate on the elimination of calcium in the urine of healthy children and in cases of calcuria. ER. SCHIFF AND E. STRANSKY. *Jahrb. Kinderheilk.* (iii) **43**, 205-9(1920).—Further investigations have confirmed the increase (from 3 to 4 times) in the elimination of Ca in the urine of normal children after subcutaneous injection of MgSO₄; this increase is comparatively little in calcuria. Consideration of these and other observations renders it probable that the metabolic changes accompanying the loss of Ca are caused by an abnormal behavior of the Mg metabolism.

J. C. S.

Blood and metabolism studies with radium emanations. J. HAUENSTEIN. *Munch. med. Wochschr.* **68**, 809-10(1921).—Observations were made of the effect of Ra radiations on the nos. of red and white blood corpuscles and on the behavior of the individual leucocyte forms in cases of carcinoma of the uterus. Red corpuscles disintegrate and decrease in amt. under the influence of γ -rays. Leucocytes increase in no. There is a relative and abs. increase in neutrophils and a relative although not abs. decrease in

lymphocytes. No effect was observed on the large, white blood cells, and the mononuclear, eosinophilic, and basophilic cells. The metabolism expts. showed that the N content of the urine decreased markedly during and after treatment. Similar results were obtained for uric acid. Acetone and acetoacetic acid were not found. The figures for indican were abnormal and slight albuminuria was observed. J. C. S.

Review of the field of pharmacology (October to December, 1922). CARL BACHEM. *Centr. Inn. Med.* 44, 177-88, 193-7 (1923); cf. C. A. 17, 151. JULIAN H. LEWIS

The treatment of arteriosclerosis and asthma with intravenous injections of a silicic acid-iodine compound. A. KUHN. *Fortschritte Med.* 41, 75-7 (1923).—The trade name of this compd. is najosil. It contains in 1 cc. 0.01 g. Na salicylate and about the same amt. of I. It is given subcutaneously and intravenously in doses of 1 to 5 cc. Subjective improvement is noted in asthma and a lowering of blood pressure in arteriosclerosis.

JULIAN H. LEWIS

The biochemistry and chemotherapy of tuberculosis. XXI. Mercury compounds in the chemotherapy of experimental tuberculosis in guinea pigs. I. LYDIA M. DEWITT. *J. Infectious Diseases* 28, 150-69 (1921).—When a series of Hg compds. was compared as to the relation of their % of Hg and bacteriostatic action on tubercle bacilli the 4 most active ones were, in order, allylale.-(AcO)₂Hg, methylene blue-HgCl₂, fluorescein-HgCl₂, and 1-amino-2-(*p*-naphthaleneazophenylmercuric acetate)-5-sulfonic acid. When these compds. were used for treatment of tuberculosis in guinea pigs none of them actually cured the disease. All the results obtained, particularly with methylene blue-HgCl₂, justify continuation of the study of mercurials in the treatment of tuberculosis.

JULIAN H. LEWIS

Therapeutic value of two new synthetic antimony compounds in cases of granuloma inguinale. ALEXANDER RANDALL. *J. Urology* 9, 491-507 (1923).—Na, Sb, thioglycollate and triamide of Sb thioglycollate produced brilliant curative results in cases of granuloma inguinale when given intravenously. In contrast to tartar emetic it exhibited no toxic effect.

JULIAN H. LEWIS

The importance of the adrenal glands in the action of certain alkaloids. II. Strychnine on the blood picture. C. W. EDMUNDS AND P. C. LLOYD. *J. Lab. Clin. Med.* 8, 563-8 (1923); cf. C. A. 17, 2013.—The changes in the total no. of leucocytes in the dog and the relative proportions of the different varieties of white blood cells produced by strychnine are only indirectly due to strychnine. They are directly due to the epinephrine which is secreted by the adrenal glands under the influence of strychnine. The epinephrine thus secreted is not in sufficient amt. to alter the no. of red cells.

E. R. LONG

Toxicity of cocaine as influenced by rate of absorption and presence of adrenaline. E. L. ROSS. *J. Lab. Clin. Med.* 8, 656-60 (1923).—Cocaine-HCl in concn. varying from 0.125 to 1.0% was injected into the leg vein of cats which had been given a light dose of chlorotone. The rate varied from 0.0028 to 0.0230 g. per kg. per min. The m. l. d. varied with the rate of administration, increase in the rate decreasing the m. l. d. The abs. m. l. d. of cocaine-HCl for chlorotoned cats is 0.0128 g. per kg. Adrenaline markedly increases the toxicity of cocaine.

E. R. LONG

Chemotherapy. H. H. DALE. *Physiol. Rev.* 3, 359-93 (1923).—A review with bibliography, devoted especially to the theory of the action of drugs in the sp. treatment of disease, particularly the action of dyes and arsenicals. The phenomena of cure are difficult to bring within the scope of any simple type of explanation. There is a constantly increasing accumulation of evidence against the idea that curative substances act in virtue of their differential affinity for parasitic protoplasm. One is compelled to assume that the tissues of the host play an essential part in the curative action which the drug initiates, in many instances. The therapeutic efficiency of the As compds. is attributed to the liberation of As in much simpler form, slowly over a long period of time. Thus the host's tissues aid in the efficiency of the drug, and organotropism is as important as parasitotropism.

E. R. LONG

The influence of the reaction of the medium upon the disinfecting action of organic dyes. I. FLRISCHER AND S. AMSTER. *Z. Immunitäts.* 37, 327-40 (1923).—Slight changes in H-ion concn. between *p*_H 5 and 8, as a result of changes in the amts. of phosphate buffers present, affect markedly the disinfecting action of trypanflavine S, methyl green, methylene blue, Martius yellow and *p*-nitrophenol. The action of the acid dyes is increased by further acidity, and that of the basic dyes by a decrease in acidity.

E. R. LONG

Urine acidification with madder. ADOLF BAUER. *Z. Urol.* 17, 274-5 (1923).—Physiologically alk. urine becomes acid on administration of madder to the patient, an

effect lasting 48 hrs. following the use of 10 g. A dose of this size has no ill effect, and increases the antiseptic property of the urine. E. R. LONG

The calorigenic action of adrenaline chloride. W. M. BOOTHBY AND I. SANDIFORD. *Proc. Am. Physiol. Soc., Am. J. Physiol.* **63**, 407(1923).—In 58 expts. with dogs adrenaline administered intravenously in varying amts. always produced an increase in metabolism as shown by the gas exchange. Adrenaline produces a direct chem. stimulation of cellular combustion and thus causes the cells to metabolize more rapidly under its influence. The secretion of the adrenal glands under normal biol. conditions accelerates the velocity of transformation of potential into kinetic energy.

J. F. LYMAN

Reversal effects observed in experiments with sodium citrate or allied salts and autonomic drugs. WM. SALANT AND NATHANIEL KLEITMAN. *Am. J. Physiol.* **65**, 62-76(1923).—The physiol. action of citrates (*C. A.* **16**, 3710) may be reversed when administered after atropine or pilocarpine. The physiol. bearing of the observed facts is discussed. While disturbance in the Ca mechanism in the body may be an important element in the pharmacol. action of citrate, tartrate, oxalate and fluoride, it is not the sole factor in detg. their behavior.

J. F. LYMAN

The blood changes and the spleen in pilocarpine, atropine and adrenaline administration. S. TAKAORI. *Intern. Med. News* No. 1026(1922); *Japan Med. World* **3**, 105(1923).—After the intravenous injection of these substances there was a transient leucopenia, with a comparatively long-continued leucocytosis. When the spleen had been extirpated, leucocytosis developed immediately after the injection of pilocarpine. After the injection of atropine and adrenaline the blood was the same as that in the normal rabbit.

M. E. MAVER

The excretion of caffeine. K. OKUSHIMA. *J. Okayama Med. Soc., No. 396*(1923); *Japan. Med. World* **3**, 140.—O. estd. the caffeine by the pharmacol. action of the CHCl₃ ext. of the desiccated urine on the skeletal muscles of the frog. The max. excretion took place in 3-4 hrs. In 10-12 hrs. the urine was entirely free from caffeine. Cf. *C. A.* **16**, 2915.

M. E. MAVER

Bromural derivatives. S. TSURUTA. *Med. News (Japan)* No. 1110(1923); *Japan Med. World* **3**, 108(1923).—T. reports the results of the exptl. administration of derivs. of bromural in the dog. The European and Japan. varieties have the same properties.

M. E. MAVER

Intoxication and starvation. Effect of adrenaline on experimentally starving pigeons. F. ARLOING AND A. DUFOUT. *Compt. rend. soc. biol.* **88**, 1037-8(1923).—Administration of 1 mg. of adrenaline per day expedites the appearance of the effects of a diet consisting of polished rice. The time of survival under such circumstances is about 10 days shorter than when no adrenaline is given. Pilocarpine, atropine and adrenaline all seem to exert the same influence, the loss of the vago-sympathetic equil. caused by these drugs being regarded as responsible for the quick onset and evolution of the symptoms of a deficient diet.

S. MORGULIS

Effect of bitters on gastric leucopenesis. M. LOEPER AND G. MARCHAL. *Compt. rend. soc. biol.* **88**, 1058-9(1923).—Exptl. evidence is given that bitters act on gastric mucosa not merely through psychic and reflex influences but also directly, but this action is weaker than that obtained with starch, peptone or bouillon.

S. MORGULIS

Effect of cold on the influence of adrenaline. ALBERT OBRÉ. *Compt. rend. soc. biol.* **88**, 1102-3(1923).—Expts. with frogs demonstrate that in the majority of instances intense and prolonged cold produces an abnormal nervous and muscular chronaxie which is responsible for the change in the effect of adrenaline on muscular excitation. Adrenaline increases muscular chronaxie and diminishes nervous chronaxie except in the cold when the former effect is reversed.

S. MORGULIS

Quinidine in the treatment of auricular fibrillation. A. E. CLARK-KENNEY. *Quart. J. Med.* **16**, 204-35(1923).

JOHN T. MYERS

The storing of quinine by red blood corpuscles in vitro. M. AKASHI. *Arch. Schiffs-Tropen Hyg.* **27**, 12-30(1923).—Quinine is bound *in vitro* by erythrocytes of horse, rabbit and beef blood. This storing process depends upon the concn. of the alkaloid, the no. of erythrocytes and the temp. After satn. with quinine the cells lose some of it to the surrounding medium with an accompanying change in the compn. of the cell membranes and ensuing hemolysis. In the presence of an excess of CO₂ dissolved in the cell suspension the alkaloid is not taken up by the cells. Liver cells behaved similarly in the above respects. Large accumulation of quinine in the kidneys and lungs of treated animals was observed. The storing of quinine in erythrocytes of animals treated with the alkaloid could not be demonstrated. Improved methods of gravimetric and qual. analysis of quinine in tissues are detailed. W. A. PERLZWIG

The treatment of Brazilian dermal leishmaniasis with "Bayer 205." A. LINDENBERG. *Arch. Schiffs-Tropen Hyg.* 27, 64-6(1923).—While the action of the drug appears to be sp. for the lesions, its use is limited through the albuminuria ensuing with prolonged treatment. W. A. PERLZWEIG

Resistance to quinine. E. RODENWALDT. *Arch. Schiffs-Tropen Hyg.* 27, 113-4 (1923); V. SCHILLING. *Ibid* 115-8.—These 2 articles are polemic over the authors' theories of the development of resistance in strains of malaria parasites to the action of quinine. W. A. PERLZWEIG

The effects of "Bayer 205" upon the blood. SHIGEMOTO SEI. *Arch. Schiffs-Tropen Hyg.* 27, 130-42(1923).—Normal rabbits were treated with "Bayer 205" and the morphology of the blood was studied. A decrease of the no. of red cells and hemoglobin was found, reaching the max. after several days. Nucleated red cells appeared, the no. of leucocytes were unaffected, but destruction of the polynuclear cells was observed. The sedimentation velocity of the red cells was increased. The complement content of guinea-pig blood was unaffected by the administration of the drug to the animal. W. A. PERLZWEIG

The treatment of bilharziasis with antimony. J. E. R. McDONAGH. *J. Trop. Med.* 26, 119(1923).—In a comparative study best results were obtained with intravenous injections of aq. solns. of $K(SbO)C_4H_4O_6$. W. A. PERLZWEIG

Phosphorus in the treatment of dermal leishmaniasis. A. CASTELLANI. *J. Trop. Med.* 26, 194-5(1923).—An account of successful use of *oleum phosphoratum*, B. P., injected into the nodules. W. A. PERLZWEIG

Therapy and prophylaxis in the control of goiter. J. WAGNER-JAUREGG. *Wiener klin. Wochschr.* 36, 139-42(1923).—An address dealing with recent attempts to control goiter by various means of I administration particularly in those districts of Switzerland where the disease is endemic. W. A. PERLZWEIG

The treatment of syphilis with bismuth preparations. FRITZ MRAS. *Wiener klin. Wochschr.* 36, 146-7(1923).—A comparative clinical study of the therapeutic effects of several com. Bi preps. W. A. PERLZWEIG

The comparative action of digitalis and of strophanthin. D. DANIELOPOLU. *Presse med.* 31, 273-5(1923).—A clinical study. W. A. PERLZWEIG

The diuretic properties of hexamethylenetetramine. L. CHEINISSE. *Presse med.* 31, 278-9(1923).—A review. W. A. PERLZWEIG

Papaverine as a vascular drug. L. CHEINISSE. *Presse med.* 31, 498 9(1923). - Review. W. A. PERLZWEIG

A new local anesthetic. Ethyl *p*-aminobenzoylphthalamate hydrochloride. A. LECERF. *Presse med.* 31, 486-7(1923).—This new compd., which is prepd. from the Et aminobenzoate and Et phthalamate, is claimed to be wholly non-toxic, sterilizable at 120° in the autoclave, very stable, and to produce local anesthesia superior to that obtained with novocaine. The clinical experiences with this new substance appear to be very satisfactory. W. A. PERLZWEIG

The treatment of epidemic encephalitis with intraspinal injections of casein. M. ROCH. *Presse med.* 31, 496-8(1923). Several cases of epidemic encephalitis were treated with intraspinal injections of 1-2 mg. of casein in soln. The purpose was to provoke a mild aseptic meningitis and thus to increase the permeability of the walls of the spinal canal to the constituents of the blood stream. The results achieved were indifferent. W. A. PERLZWEIG

Arsphenamine-dermatitis. HANS KRONBERGER. *Wiener klin. Wochschr.* 36, 237-8(1923).—A study of the tolerance of patients to various modifications of arsenphenamine, and of the supposedly beneficent effect of suprarenine in cases of intolerance to the drug. W. A. PERLZWEIG

Clinical and pathological aspects of iodine therapy in arteriosclerosis. J. WIENSEL. *Wiener klin. Wochschr.* 36, 252-6(1923).—A clinical lecture. W. A. PERLZWEIG

Anaphylactoid rheumatism. JULIUS BACER. *Wiener klin. Wochschr.* 36, 256 8 (1923).—An address. W. A. PERLZWEIG

The therapeutic use of iodine in goiter. N. JAGIC and G. SPENGLER. *Wiener klin. Wochschr.* 36, 264-5(1923).—Favorable clinical results of I treatment of goiter and of various forms of Basedow's disease are reported. W. A. PERLZWEIG

The influence of hyperpyretic substances upon the fever curve. PAUL SAXL. *Wiener klin. Wochschr.* 36, 272-3(1923).—Chills may be induced in febrile conditions by intravenous, but not subcutaneous, injections of certain protein and protein-split products (vaccines, "Kaseosan," deutero-albumose) and of org. and inorg. non-protein substances ("Sanarthrit," lactose, dextrose, NaCl, and solns. and suspensions of salts of heavy metals). In normal afebrile subjects these substances produce a rise of temp.,

but no chill. While the induced chill may or may not be accompanied by a great rise of temp., the temp. usually falls to normal after the subsidence of the chill. Certain substances (foreign serum, CaCl_2 , "Afenil") do not cause any chill when injected intravenously into febrile patients. Other substances (Na nucleinate, "Electrokollargol," "Vakzineurin") when injected intramuscularly produce rise of temp. without chills. The application of these observations to the treatment of febrile infectious conditions is discussed.

W. A. PERLZWEIG

Diuresis experiments on normal children controlled by a definite food concentration. A. F. HECHT. *Wiener klin. Wochschr.* 36, 449(1923).—Normal children and infants after being placed upon standard diets with a definite H_2O content and with well established urinary excretion curves showed no diuresis upon administration of caffeine, some showing a diminution of urine elimination. The administration of "Diuretin" similarly failed to produce diuresis in normal children. "Novasurol" on the other hand caused marked and regular diuresis. The administration of pituitrin to children with nervous polyuria served to diminish materially the daily urinary output.

W. A. PERLZWEIG

The mechanism of the action of arsenic upon protoplasm. C. VOEGTLIN, H. A. DYER and C. S. LEONARD. *U. S. Pub. Health Repts.* 38, No. 33, 1882-1912(1923).—Reduced glutathione, thioglycolic acid, α -thiolactic acid, glycylcysteine and thiosalicylic acid counteract the toxic action of As compds. of the structure $\text{RAs}=\text{O}$ on trypanosomes *in vitro* and in the blood of rats. The appearance of symptoms and the time of death are greatly delayed. Disulfides of the structure $\text{R}_2\text{S}-\text{SR}$ are much less effective or without effect. The antitoxic effect is specifically due to the SH group which reacts chemically with the As compd. All cells, including those of trypanosomes, contain an SH compd., possibly glutathione. When the amt. of As furnished to the cells exceeds a certain limit, poisoning and death will follow because the abs. amt. of SH compds. will be reduced below the physiol. requirement. But if the cell is given an extra supply of SH compds., the reduction below the physiol. requirement will not occur and the protoplasm will escape injury. The chemotherapeutic action of As is discussed. Glutathione and some other SH compds. are concerned in certain biological oxidations and reductions. A new compd., 3-amino-4-hydroxyphenylarsenious-bismonothioglycolic acid, was prepd. as follows: 7 g. 3-amino-4-hydroxyphenylarsenious-oxide-HCl are mixed with 11 g. thioglycolic acid. The mixt. is heated on a water bath, dried in a desiccator, and the gummy mass is washed with Et_2O and dissolved in abs. alc. The alc. is removed *in vacuo*, and the residue is further washed with Et_2O , dried in a desiccator and pulverized. The compd. analyzed 1.12% high in As and 2.16% excess of S. It was 94.23% pure. This compd. is insol. in H_2O , Et_2O and cold mineral acids; sol. in alc. and alkali. In equimol. doses, it showed a marked delay in parasitocidal action as compared with arsenoxide. The results add further proof to the theory of As action stated above.

CHAS. H. RICHARDSON

Poisoning by *Narcissus incomparabilis* Mill. E. MARTIN-SANS and DEVERBIZIER. *Bull. sci. pharmacol.* 30, 265-6(1923).—*N. incomparabilis*, which is apparently a fixed hybrid between *N. pseudo-narcissus* and *N. poeticus*, has shown toxic properties. It is probable that this toxicity is general for all the species of *Narcissus* which contain an alkaloid in their tissues.

I. W. RIGGS

Physiologic testing of adrenaline. Natural adrenaline prepared by G. Bertrand. L. LAUNOY. *Bull. sci. pharmacol.* 30, 325-36(1923).—The natural cryst. adrenaline, prepd. by G. Bertrand, when injected intravenously into rabbits in const. doses, causes phenomena which are sensibly const. Among these phenomena is death within 15 min. of a male rabbit of 2 kg. wt., following a dose of 0.00025 g. per kg. The constant of toxicity is accordingly 0.00025. The cardio-vascular constants are in 4 grades following doses of 1, 5, 15 and 50 thousandths of 1 mg. The max. hypertension in mm. of Hg produced by these doses were 30, 60, 90 and 110, resp., and the max. durations in sec. of the hypertension were 45, 90, 180 and 270, resp. These figures may serve as bases in the investigation of other adrenaline.

I. W. RIGGS

Action of thorium X on the catalase of the liver. ALFRED MAUBERT, LEON JA-LOUSTRE and PIERRE LEMAY. *Compt. rend.* 176, 1502-5(1923).—The catalase used was prepd. according to Bertrand and Thomas and was dild. for the tests 1 to 7000. The catalase was allowed to act on H_2O_2 alone and in the presence of Th X, the concn. of the latter ranging from 0.1 microgram up to 200 γ . It was proved that Th X had no action on H_2O_2 in the absence of catalase. It was found that Th X in small doses activates catalase of the liver but in large doses paralyzes the catalase. This action is caused by the α -radiation. The Th emanation generated solely from α -rays acts the same as Th X.

I. W. RIGGS

Action of insulin on hyperglucemia and on acidosis. A. DESGREZ, H. BIERRY AND F. RATHERY. *Compt. rend.* 176, 1833-6(1923).—Expts. were made with the active principle of the pancreas prepd. by the authors in the form of exts. and in the form of a white powder free from fats and salts. The results confirm those of Banting and his co-laborers.

L. W. RIGGS

Pharmacodynamic action of the insecticide from the flowers of pyrethrum. J. CHEVALIER AND FERNAND MERCIER. *Compt. rend.* 176, 1847-8(1923). The toxic action of *Chrysanthemum cinerariaefolium* and allied species is due neither to an alkaloid nor glucoside but to an oleoresin in the form of an ester which is easily saponifiable, and the free acid of which is toxic but to a less degree. This ester is extd. from the entire plant by cold alc. and sepd. from the waxes, resins and other impurities by extn. with Et₂O and with petroleic ether. It is insol. in water and in tests upon animals was used in the form of gummy emulsions. This substance is toxic to cold blooded animals, much less toxic to warm-blooded animals and harmless to man. Its action upon the muscles is similar to that of veratrine but different toward other bodily functions. It is proposed that pyrethrum be used as an insecticide in preference to As and Ph compds.

L. W. RIGGS

Pharmacodynamic action of the insecticide principle in pyrethrum flowers. A. JUILLET. *Compt. rend.* 177, 294-6(1923); cf. Chevalier and Mercier, preceding abstr. The petroleic ether ext. of recently collected dry flowers of *Chrysanthemum cinerariaefolium* Vis. was evapd. to a sirup and treated successively with 10% solns. of Na₂CO₃, (NH₄)₂CO₃ and NaOH. These solns. were neutralized with 0.1 N H₂SO₄ and extd. with Et₂O when a feebly acid product was obtained which was very toxic to insects. The resin isolated by Chevalier and Mercier is not considered a new substance but a mixt. having the same toxic action as the pyrethrone of Fugitani or the pyrethol of Sato.

L. W. RIGGS

Toxicity of a polymer of hydrocyanic acid. CIT. BEDEL. *Compt. rend.* 176, 1927-9 (1923).—A hypodermic dose of 0.028 g. per kg. of body wt. of (HCN)_n had little or no action upon a guinea pig (0.0032 g. of HCN being fatal in 20 min.). By the mouth a dose of 0.75 g. of (HCN)_n per kg. was fatal, which shows its comparative low toxicity. The symptoms of poisoning resemble those from poisoning with HCN and are due to a transformation of (HCN)_n in the organism with the regeneration of HCN.

L. W. RIGGS

Aniline dyes in therapeutics. JOHN W. CHURCHMAN. *J. Am. Med. Assoc.* 79, 1657-60(1922).—The behavior of bacteria toward gentian violet follows closely the Gram reaction. This is also true of other triphenylmethane dyes, among them magenta. Toward acid fuchsin (a sulfonated trimethylmethane) the behavior of bacteria is in certain respects the exact reverse of their behavior toward the basic dyes. Thus if bacteria are exposed to acid fuchsin and planted on plain agar, the Gram-positive spore bearing aerobes survive and the commoner Gram-negative bacteria die. This fact is applied to the sepn. of cultures of the 2 forms of bacteria. This reversal is accounted for by the presence of the sulfonic acid group. From tests upon surgical infections it appears that the aniline dyes, and other substances, exercise a selective sterilization upon bacteria. Thus acid fuchsin kills *B. pyocyaneus*, an organism which is almost unaffected by gentian violet.

L. W. RIGGS

Insulin: its action, its therapeutic value in diabetes, and its manufacture. IN SULIN COMM. OF THE UNIV. OF TORONTO. *J. Am. Med. Assoc.* 80, 1847-51(1923). Diabetes mellitus is considered a disease of metabolism in which carbohydrate is not efficiently utilized by the body thereby causing a derangement of the normal metabolism of the proteins and fats as well as carbohydrates. An ext. of pancreas under the name *insulin* has been proved to have the following named actions: (1) Insulin lowers the blood sugar in normal rabbits; characteristic symptoms supervene when a certain low level is reached, and these symptoms are specifically antidoted by glucose. (2) It may prevent the hyperglucemia due to pitdure, asphyxia, adrenaline and ether. (3) It increases the sugar consumption by the isolated mammalian heart. (4) It causes glycogen to be deposited in the liver of diabetic animals fed with sugar. (5) It raises the respiratory quotient of diabetic animals fed with sugar. (6) It affects the migration of fat in diabetic animals. (7) It causes the accione bodies to disappear from the urine of diabetic animals. The therapeutic use of insulin in diabetes mellitus is described at length. Toxic symptoms result from excessive doses of insulin; these symptoms are relieved by giving glucose. Patents are held by the Univ. of Toronto for the purpose of controlling the manuf. and the prevention of com. handling of insulin. Reliable mfg. firms will be licensed under these patent rights by the Univ. of Toronto, the object being to insure a product of uniform quality and potency at a min. cost. Use of insulin in diabetes mellitus. W. H. OLMSTED AND S. H. KAHN. *Ibid* 1903-7.—In observations on more

than 40 patients the action of insulin was noted with reference to glucosuria, acetoneuria, blood sugar, N balance, and total metabolism, also in 4 surgical cases. The findings are assembled in 10 tables. The results are favorable to the intelligent use of insulin.

L. W. RIGGS

Therapeutic application of *Bacillus acidophilus* milk. H. A. CHEPLIN, H. C. FULMER AND C. O. BARNEY. *J. Am. Med. Assoc.* 80, 1896-9(1923).—*Bacillus acidophilus* milk prep'd. according to the method of Cheplin and Rettger and enriched by 50 to 100 g. of lactose was given to the amt. of one l. daily in 3 equal doses from 2 to 3 hrs. after ordinary meals to 10 patients. The patients were suffering from chronic constipation or mucous colitis. It was found that *B. acidophilus*, when given by mouth in the form of min. amts. of milk cultures, lends itself to complete implantation and colonization within the human digestive tract, effecting a complete simplification of the fecal flora, and supplanting almost all known intestinal toxigenic microbes. In chronic constipation, there was marked clinical improvement in the toxic symptoms and regulation of fecal eliminations from the bowel. In mucous colitis, beneficial changes were noted with daily natural defecations free from any mucus.

L. W. RIGGS

Action of calcium in experimental cocaine poisoning. IRA FRANK, J. F. STRAUSS AND WM. A. SMILEY. *J. Am. Med. Assoc.* 80, 1908-9(1923).—The statement of Mayer (cf. *J. Am. Med. Assoc.* 77, 1336(1921)) that Ca acts antagonistically to the toxic effects of cocaine by overcoming the depression of the medullary centers caused by cocaine could not be confirmed by expts. on rabbits. The results obtained do not warrant the use of Ca lactate or chloride as a reliable therapeutic measure in acute cocaine poisoning.

L. W. RIGGS

Precipitin reaction of thyroglobulin. Presence of thyroglobulin in the thyroid lymph of goitrous dogs. LUDWIG HEKTOEN, A. J. CARLSON AND KAMIL SCHULHOF. *J. Am. Med. Assoc.* 81, 86-8(1923); cf. *C. A.* 17, 1653.—Expts. with dogs demonstrate in the thyroid lymph a thyroid product (thyroglobulin) which probably constitutes or contains the thyroid hormone. As these tests were made on hyperplastic thyroids, they should be repeated on dogs with normal thyroids. It remains to det. also whether the blood coming from the thyroid gland contains less thyroglobulin than the thyroid lymph. The precipitin test may furnish a useful index of physiologic and pathologic variations in thyroid activity, in animals under exptl. conditions as well as in man, especially in cases of ligation (artery and veins) of the superior thyroid poles under local anesthesia. For details in prep. dog thyroglobulin, thyroid lymph, and in making the test, the original paper should be consulted.

L. W. RIGGS

The use of *Bacillus acidophilus* milk in a tuberculosis sanatorium. WM. H. MORRIS. *J. Am. Med. Assoc.* 81, 93-7(1923).—In 18 out of 22 tuberculous patients with gastrointestinal disorders the daily use per pateint of 1 quart of milk, inoculated with *B. acidophilus*, from periods ranging from 10 days to 7 months resulted in complete relief or various grades of improvement in the gastrointestinal symptoms. Four of the 22 patients had constipation and received in addn. to the milk 50 or 100 g. of lactose daily. There was an improvement in 3 of these 4 patients. The no. of cases are considered too small to warrant definite conclusions.

L. W. RIGGS

Standardization of digitalis by its action on the human heart. Preliminary report H. E. B. PARDEE. *J. Am. Med. Assoc.* 81, 186-8(1923).—The method of procedure was as follows: (1) A control electrocardiogram was taken between 4 and 5 p. m. (2) The test dose was given by mouth in about 60 cc. of water at 7 a. m. of the day following. (3) A record was taken between 4 and 5 p. m. of this day to see whether or not the test dose had produced an effect. (4) A larger dose was given by mouth at 7 a. m. of the next day, of sufficient size to bring the total up to 1 minim per pound of the patient's wt., plus another 20 minims, which was to make up for the 24 hrs. excretion of the drug. (5) A third record was taken between 4 and 5 p. m. of this day to ascertain whether this large dose had affected the electrocardiogram, for only if it had done so could it be known that the patient was normally susceptible to the drug. (6) Later doses and later records were used to follow the course of digitalization, especially in resistant patients who showed no effect after the large dose. The max. change in the T wave of the electrocardiogram was considered the max. effect of this dose.

L. W. RIGGS

Insulin in tissues other than the pancreas. Preliminary communication. C. H. BEST AND D. A. SCOTT. *J. Am. Med. Assoc.* 81, 382-3(1923).—Banting and Best found that exts. of the thyroid and of thymus, by the methods that were used in extg. insulin, caused distinct but transient lowerings of the blood sugar. The authors have made exts. of the liver, spleen, thyroid, thymus, submaxillary gland and of other tissues. These exts. repeatedly tested with normal rabbits consistently produced a marked lowering of the blood sugar of these animals. Large doses produced typical insulin con-

vulsions and the convulsions were alleviated by the administration of dextrose. Under certain conditions a substance resembling insulin is excreted in the urine. Insulin was present in every tissue investigated by the authors. L. W. RIGGS

Insulin treatment of postoperative (non-diabetic) acidosis. WM. THALHIMER. *J. Am. Med. Assoc.* 81, 383-5(1923).—Injections of insulin and glucose solns. in 3 cases of postoperative vomiting and ketosis apparently cleared up these conditions much more rapidly than with injections of glucose solns. Insulin therapy must be given and controlled even more carefully in cases of this type than in diabetes.

L. W. RIGGS

The phagocytosis of lead compounds and their influence on the activity of the leucocyte. J. FINE. *J. Ind. Hyg.* 5, 138-44(1923).—The methods of W. O. Fenn (cf. C. A. 17, 1252) were employed. **Conclusions:** Metallic Pb is less readily phagocytized than is basic lead carbonate. The presence of sol. Pb injures the leucocyte, as is demonstrated by its diminished ability to engulf C particles. In the presence of metallic Pb the phagocytosis of C is retarded. This is probably due to the toxic effect of sol. Pb present in soln. The rate of phagocytosis of metallic Pb by leucocytes is of the same low order of magnitude as that of quartz. These facts suggest that, like quartz, metallic Pb remains as a foreign body in the lung and excites fibrosis.

L. W. RIGGS

Pharmacological efficacy of digitalis leaf. MASAO WATANABE. *Tohoku J. Exptl. Med.* 4, 98-148(1923).—The method of estg. the efficacy of digitalis preps. is as follows: The excised auricle of a frog heart is kept alive in Ringer soln. at 25°, a given quantity of the drug to be tested is added and the time needed to cause the standstill of the auricle is observed, next the quantity of strophanthin which is needed to produce the standstill in the same length of time is detd.; this quantity expresses the value of the pharmacol. efficacy of the drug. In using this method it was found that the efficacy varied with the species, the part of the plant used, the year of growth, the season of the year, the fertilizer used and the locality where grown. The efficacy varied greatly with the methods of curing and preserving the drug. The keeping qualities of digitalis drugs and the influence of the digestive juices upon the drugs were studied.

L. W. RIGGS

Action of drugs on blood pressure, especially the venous pressure. MICHINOSUKE YOKOTA. *Tohoku J. Exptl. Med.* 4, 23-51(1923).—Expts. with dogs were made to det. the actions on the blood pressure of H_2O , H_2O_2 , $CHCl_3$, urethan, $AmNO_3$, $NaNO_3$, $CCl_3CH(OH)_2$, chlorotone, As_2O_3 , arsenites, arsenates, morphine, strychnine, picrotoxin, adrenaline, pituitrin, peptone, histamine, digitalis compds, strophanthin and Ba salts. These expts. are described with much detail and the actions of the drugs are illustrated by 17 kymographic diagrams. The summary fills 2 pages. **Action of aconite on the peristalsis of the stomach.** *Ibid* 52-7.—Expts. were made with dogs to test the action of aconite on the stomach *in situ* and on stomach tissue freshly prepd. and placed in Ringer soln. at body temp. Aconite excites the Auerbach plexus as well as the vagus terminals but not the sympathetic terminals. When it is resorbed it checks stomach peristalsis by its irritation of the ganglionic cells. As this action is stronger than that before mentioned, the peristalsis after resorption of the drug is still more diminished.

L. W. RIGGS

Cardiac-tonic and diuretic action of kobu (*Laminaria japonica* Aresch). MASAO WATANABE. *Tohoku J. Exptl. Med.* 4, 149-65(1923).—The kobu plant (a sea-bottom plant) contains iodides, mannitol, protein and fibrous matter. The blade of this plant has long been used for food in Japan and as a cardiotonic in China. Expts. were made with frogs and with rabbits using a 10% decoction and also an alc. ext. Kobu has a cardiotonic and vasodilative action. Quick administration into the circulation of a small quantity causes a slight preliminary fall of the blood pressure followed by a subsequent rise. But when it is administered very slowly there is only a rise of blood pressure. The dilatation of blood vessel, and the consequent decrease of peripheral resistance together with the simultaneous rise of blood pressure accelerates the circulation of blood in various organs. The popular use of this plant as a cardiotonic has some pharmacol. grounds. Kobu induces diuresis partly by its cardiotonic and vasodilative actions and partly from the diuretic action of the mannitol present. Thus, though kobu contains some heart poison, it is daily used as a common foodstuff without producing any known instance of intoxication. This is chiefly due to the largeness of its lethal dose, which for the rabbit is 50 g. per kg. of body wt. With frogs kobu paralyzes the central nervous system, augments the heart beat and contracts the blood vessels. This paralysis is due to the watersol. component of the active principle of kobu, while the cardiotonic and vasoconstrictive action are induced by the ether sol. component. The cardiotonic

action is weakened by the water-sol. component and strengthened by mannitol.

L. W. RIGGS

The influence of the medium on the toxicity of certain alkaloids towards protozoa. T. A. HENRY AND H. C. BROWN. *Trans. Roy. Soc. Tropical Med. Hyg.* 17, 61-71 (1923).—Expts. *in vitro* were made to test the toxicity of quinine, emetine and conessine (from *Holarrhena* bark) upon the protozoa obtained from hay infusion. The solns. of the alkaloids were made of various degrees of acidity or alkali by the addn. of very dil. standard HCl or NaOH. The results show that the toxicity of the alkaloids named toward the protozoa used is considerably increased in an alk. medium. It is possible that if this condition can be realized *in vivo*, the action of these alkaloids in protozoal diseases may be made more certain and efficient. These results confirm Schaeffer's observations that quinine dihydrochloride (acid) is less active than quinine monohydrochloride (neutral), and emphasize Acton's suggestion that for injection quinine base would probably be more efficient and possibly non-irritant, if a means can be devised for injecting it in solu. in this form.

L. W. RIGGS

Influence of narcotics of the paraffin series on the swelling of cell colloids. (A contribution to the theory of narcosis.) M. KOCHMANN. *Biochem. Z.* 136, 49-65 (1923).—A series of 0.75% NaCl solns. was prepd. contg. each narcotic in a range of concns. In the stronger solns., swelling occurs, in the more dil. solns., dehydration. In order of effectiveness in producing either change, the narcotics stand: (1) CHCl_3 , (2) $\text{CCl}_3\text{CH}(\text{OH})_2$, (3) $\text{C}_6\text{H}_{11}\text{OH}$, (4) Et_2O , (5) $\text{C}_4\text{H}_9\text{OH}$, (6) $\text{C}_2\text{H}_5\text{OH}$, (7) EtOH , (8) MeOH , (9) $\text{CO}(\text{NH}_2)\text{OC}_2\text{H}_5$. Frog gastrocnemius shows a diminished vol. in those solns. narcotically effective for it, and a return to normal when transferred to 0.75% NaCl soln. The order of effectiveness for gastrocnemius is the same as for fibrin, except that Et_2O shifts to (6) and urethan to (7). The narcotic power of a given substance is detd. by 2 classes of properties: (a) *prerequisite*, e. g., lipid soly., slight soly. in H_2O , lowering of surface tension, adsorption by cell colloids; (b) *specifically narcotic*, depending on dehydration. This causes diminished cell permeability and hence irritability. With the fibrin solns. class *b* only holds; with the muscle preps. class *a* is concerned as well. Hence the change in position of Et_2O and urethan.

GEORGE ERIC SIMPSON

The physiological action of amino acid esters. MINORU ARAI. *Biochem. Z.* 136, 203-12 (1923).—By tying up the CO_2 group of the amino acids can an approach, in physiol. action, to the amines, in which the CO_2 group is entirely lacking, be effected? To answer this, the influence of the HCl salts of the esters on blood pressure, and on the contraction of isolated strips of uterus and intestine, is detd. The Me ester of *L*-histidine is quantitatively weaker, but similar, to histamine. The Et esters of *L*-tyrosine, *D,L*-phenylalanine, *L*-leucine, *L*-cystine, and glycocoll are more or less active, although the acids themselves are indifferent. Thus the mode of action of the esters is more or less like that of the corresponding amines.

GEORGE ERIC SIMPSON

The chemistry and mode of action of gray ointment. HELLMUT MENSCHEL. *Biochem. Z.* 137, 193-200 (1923).—Certain com. preps. of gray ointment contained varying amts. of total Hg as Hg soaps (0.7-4.7%) increasing with age. A guinea pig died after 10 days treatment with 10 g. of an Hg-soap prepn. contg. a total of 0.6 g. Hg, but no metallic Hg. In the liver, brain, lungs and kidneys, Hg was found in greater amts. than previously reported (liver and brain about 5 mg. each). Hüsgen's procedure was used. In previous investigations the analytical procedure has been inadequate.

GEORGE ERIC SIMPSON

The stability of adrenaline hydrochloride in various solutions. D. VAN DER HOOF AND C. C. HASKELL. *Am. J. Med. Sci.* 166, 119-25 (1923).—The ability of adrenaline to retain its potency when made up in a variety of substances commonly employed as diluents was detd. In borolyptol the pressor action had almost entirely disappeared within $3\frac{1}{2}$ hrs., and in glycethymoline the rate of deterioration was much the same. In Dobell's soln. there was a definite loss within 24 hrs. and after 1 week the soln. was inert. In physiol. saline little or no loss in pressor action took place within the first month but the soln. was inert after 59 days. Adrenaline maintained its potency in listerine for 19 days, in antiseptic soln. N. F., for 4 months. Apparently the preservative action of listerine is associated with the benzoic acid present.

G. H. S.

Quantitative studies in syphilis from a clinical and biological point of view. III. Arsenical content in scales, blood, and urine in arsenical and non-arsenical eruptions. J. A. FORDYCE, ISADORE ROSEN AND C. N. MYERS. *Am. J. Syphilis* 7, 209-24 (1923); cf. *C.A.* 17, 2608.—When normal elimination of As through the skin is interfered with its deposition in the cutaneous layers is sufficient to produce irritation and consequent edema which prevents the functioning of the epidermis and results in an exfoliating

dermatitis. In the scales from 20 of 22 cases of syphilis with a desquamating rash after arsenical treatment As was found in amts. varying from 0.123 mg. to 315.9 mg. per 100 g. of material. Analyses of the blood and urine gave several instances in which the blood failed to show As in determinable amt. while it was present in the urine in considerable quantity. IV. Arsenic content in the blood at various intervals after intravenous injection of arsphenamine. *Ibid* 225-86. - Immediately after the injection 60% of the As has been localized outside of the blood stream, and this is the time of max. concn. of As in the blood, a value of 4.21 mg. of metallic As being present in 100 g. of dried material. The amt. of As in the blood gradually diminishes. The rate of division of As between blood and tissues varies in different individuals. Persons with an As idiosyncrasy show abnormal values for the blood As. G. H. S.

Clinical and biochemical study of neurosyphilis. I. Arsenic content of the spinal fluid after the intravenous administration of silver arsphenamine. I. H. CORNWALL AND C. N. MYERS. *Am. J. Syphilis* 7, 287-317 (1923). Within 2 hrs. of the intravenous injection of Ag arsphenamine As may be found in the spinal fluid in amts. as large as 143 mg. per 100 g. of dried specimen. Usually the amt. present decreases after the first 2 hrs., rises slightly between 24 and 48 hrs., and reaches a new high point at 72 hrs., when it may be found in amts. as large as 192 mg. per 100 g. of material. G. H. S.

Sulfarsenol in the treatment of syphilis. S. IRELAND. *Am. J. Syphilis* 7, 318-22 (1923).—Sulfarsenol ($C_{14}H_{14}O_8As_2N_2Na$) used subcutaneously or intramuscularly gives therapeutic results comparable to those obtained with neoarsphenamine, as judged by the effects on the cutaneous lesions. G. H. S.

Mercury inhalation therapy of syphilis. III. Shall it be condemned? JACOB GUTMAN. *Am. J. Syphilis* 7, 326-46 (1923); cf. *C. A.* 17, 2006. IV. Mercury versus arsphenamine in the treatment of syphilis. *Ibid* 347-51. The use of Hg is advocated. G. H. S.

Toxicity and trypanocidal activity of tartrobismuthate and its relation to the treatment of syphilis. C. N. MYERS AND H. B. CORRIE. *Am. J. Syphilis* 7, 352-76 (1923).—As an antiluetic Bi is inferior to the arsenicals. There appears to be a synergistic action of Bi and As which may be of therapeutic significance. G. H. S.

Biological evaluation of Filix mas. R. WASICKY. *Arch. exptl. Path. Pharmacol.* 97, 454-61 (1923).—The biol. method for detg. potency, i. e., by the exposure of fish to definite concns., is more trustworthy than the usual chem. methods. G. H. S.

Action of fluorine. HERMANN WIELAND AND GERTRUD KREIZAHN. *Arch. exptl. Path. Pharmacol.* 97, 489-98 (1923).—The activity of Na fluosilicate depends upon the fact that within the body the substance liberates F ions, and the toxic effects are manifest because these ions combine with the Ca in the tissues. HF is a caustic poison primarily because of the intact HF mols., rather than because of the acid character. G. H. S.

Comparison of the actions of *d*-, *l*-, and *i*-camphor. V. Electrographic studies with the isolated frog heart. G. JOACHIMOGLU AND E. MOSLER. *Arch. exptl. Path. Pharmacol.* 98, 1-11 (1923).—The 3 isomers of camphor produced comparable changes in the electrogram of the isolated frog heart. G. H. S.

Influence of pilocarpine, atropine, and adrenaline upon the insensible perspiration. ORRO MOOG. *Arch. exptl. Path. Pharmacol.* 98, 75-90 (1923).—The subcutaneous administration of pilocarpine increases the amt. of insensible perspiration, with the external temp. at 23-5°, an effect most probably due to a stimulation of the parasympathetic nerve endings of the sweat glands. There is no adequate proof that the increase in insensible perspiration is fundamentally a phys. evapn. process directly dependent upon vascular dilatation. Atropine diminishes the excretion, when the drug is given by intramuscular injection; when given orally it is without influence. Adrenaline, given either subcutaneously or intramuscularly, preceptibly diminishes the insensible perspiration, doubtless through the effects of vasoconstriction. G. H. S.

Modifications in the vascular actions of strophanthine by antimony, potassium and calcium. HELENE GRUMACH. *Arch. exptl. Path. Pharmacol.* 98, 123-8 (1923).—The increased action of strophanthine upon the frog heart and muscle during intoxication by heavy metals (Cu, Sb) extends also to the vascular system. Under like conditions the vessels are more sensitive than the heart. G. H. S.

Intensifying the action of medicinal mixtures, with particular reference to novocaine and potassium sulfate. O. GROS AND M. KORTMANN. *Arch. exptl. Path. Pharmacol.* 98, 129-47 (1923).—When united in a suitable mixt. novocaine chloride and K_2SO_4 show an action upon the frog nerve prep. exceeding the effect of the substances separately. G. H. S.

Tolerance to arsenic. FRITZ KÜBLER. *Arch. expil. Path. Pharmacol.* 98, 185-97 (1923).—By long-continued treatment with As_2O_3 , dogs were rendered tolerant to normally lethal doses. In the tolerant condition the elimination of As by the urine is diminished, the reduction being related to the amt. administered, and under certain conditions only 0.3% of the quantity introduced is so excreted. Under other circumstances a dog receiving 20 mg. per day will eliminate more As than will a dog receiving 800 mg. Both the percentage and the abs. diminution in excretion are to be referred to a decreased absorption through the intestine. As which is absorbed is eliminated exclusively through the kidney, and a significant retention never occurs. Tolerance to As once developed persists for a very long time, and it can be disclosed some time later by a renewed feeding of the compd. The explanation of the tolerance is to be found solely in the conditions in the intestinal tract, for the dogs tolerant to As are as sensitive as are normal dogs to the compd. when administered subcutaneously.

G. H. S.

Fixation of atropine in the rabbit and its relation to non-specific stimulation. ERICH HESSE. *Arch. expil. Path. Pharmacol.* 98, 238-52(1923).—The agent in rabbit serum which detoxicates atropine is composed of two fractions, one thermostable and another thermolabile and specific. The effect appears to resemble an enzyme action in which the hypothetical bodies resemble a pro- and a co-enzyme. Rabbit serum is also active on cocaine. The treatment of rabbits with milk, a foreign serum, gelatin, etc., did not modify the detoxicating power. The non-specific effects of injections of colloidal S, protargol, oil of turpentine, etc., are shown by the fact that shortly after the injection the inactivated serum is as effective in destroying atropine as was the native serum.

G. H. S.

Influence of pyrimidone on metabolism. HANS GESSLER. *Arch. expil. Path. Pharmacol.* 98, 257-87(1923).—Pyrimidone modifies several metabolic processes in a characteristic manner: It reduces protein exchange and heat production, and causes a retention of water and of NaCl.

G. H. S.

Colloid chemistry of the mode of action of some diuretics. I. B. STUBER AND A. NATHANSOHN. *Arch. expil. Path. Pharmacol.* 98, 298-320(1923).—A discussion of the physico-chem. properties of some of the diuretic substances.

G. H. S.

Quantitative action of homologous quaternary aliphatic ammonium bases. FRITZ KÜLZ. *Arch. expil. Path. Pharmacol.* 98, 339-69(1923).—The iodides of trimethyl and triethylalkylammonium bases were investigated as to their quant. action upon the motor nerve endings and upon the cardio-inhibitory app. The curves of action of the trimethyl and triethylalkyl series did not run parallel as regards the curare effect. In the triethyl series the first two members were of the same potency; the rest became increasingly strong with lengthening of the side-chain. In the trimethyl series the activity diminished from the Me to the Pr compds. The butyl compd. was about 10 times more active than the Pr, and from this member of the series the activity decreased but slowly (the hexyl compd. was not tested). Only the first 5 members of the series stimulated the cardio-inhibitory app. This muscarine action is most marked with the butyl compd. All of the members of the triethylalkyl series show an atropine effect.

G. H. S.

Quantitative studies on the fate of nicotine in the body after tobacco smoking. PAUL NOETHER. *Arch. expil. Path. Pharmacol.* 98, 370-7(1923).—After the subcutaneous injection of nicotine into guinea pigs the substance was found (after 6 hrs.) in the greatest concn. in the urine, with a considerable amt. in the intestine, and detectable amts. in the liver and lungs. After parenteral introduction nicotine appears in the urine within $1\frac{1}{2}$ hrs. and continues to be eliminated by the kidney up to about 10 hrs. After smoking, considerable amts. of nicotine quickly appear in the urine, the time of elimination being about the same regardless of the smoking habits of the individual. There is no evidence of an accumulation of nicotine in the body, and during the night the body again becomes nicotine free.

G. H. S.

Quinidine in auricular fibrillation. A. J. BOEKELMAN. *Arch. ges. Physiol.* (Pflüger's) 198, 615-32(1923).—Upon the isolated rabbit heart quinidine causes retardation of both auricle and ventricle, a diminished contraction, more marked in the ventricle than in the auricle, a decreased sensitivity to faradic stimulation, a lengthened conduction time. Washing the heart treated with quinidine with Locke-Ringer soln. shows that the action is only partially reversible, and the reversibility is not materially modified by increasing the Ca of the washing fluid. Atropine does not modify the action of quinidine upon the isolated heart.

G. H. S.

Modifications in toxic actions by lecithin. HANS BREUER. *Arch. ges. Physiol.* (Pflüger's) 199, 57-87(1923).—The toxic action of many compds., including morphine,

camphor, and digitalis, is weakened by large amts. of lecithin. When the toxic substance and lecithin are simultaneously administered the action is particularly pronounced. The preliminary administration of lecithin, within certain time limits, also diminishes the effect of the drug subsequently given, but the action here is less marked. Small amts. of lecithin, on the contrary, frequently, but not always, intensify the toxic actions. For demonstrating such effects the properties and mode of prepn. of the lecithin are very important, since a great variation is seen in different preps. Egg lecithin has a greater detoxicating action than lecithin from horse brain. The effectiveness of a lecithin can be estd. by detg. its action in combination with digitalis on the frog heart. These relationships between large and small amts. of lecithin and toxic actions suggest that the lipoids play a role in the transfer of the toxic substances from the blood plasma to the nervous tissue.

G. H. S.

Therapeutic action of vacine dihydrochloride, intraspinally administered, in meningitis. H. BIRKHOLZ. *Arch. Ohren-, Nasen-, u. Kehlkopfheilk.* 109, 112-44 (1922).—Vacine dihydrochloride (isoctylhydrocupreine) is ineffective in the intrathecal therapy of streptococcal meningitis. Within 8 hrs. of the time of injection the vacine had completely disappeared from the spinal fluid. Resorption is so rapid that the substance cannot be maintained for any appreciable length of time in the spinal canal in an effective germicidal concn.

G. H. S.

Therapy of surgical tuberculosis with lecetyl. GERHARD DEFTMANN. *Beitr. klin. Chir. (Bruns')* 128, 90-5 (1923).—The essential ingredient of lecetyl is Cu. The substance has a sp. action on tuberculous tissue, causing necrosis and sloughing, and appears to be decidedly beneficial in surgical tuberculosis.

G. H. S.

Bromural and adaline intoxication; effect on the eye. C. H. SATTLER. *Klin. Monatsbl. Augenheilk.* 70, 149-52 (1923).—Continued use of bromural (bromoisovaleryl-anilurea) or adaline (bromodiethylacetylurea) leads to an intoxication involving damage to the vision.

G. H. S.

Injury to the cornea by hydrogen sulfide. G. F. ROCHAT. *Klin. Monatsbl. Augenheilk.* 70, 152-4 (1923).—Exposure of the eyes to H_2S results in the development of minute multiple erosions of the cornea.

G. H. S.

Bilateral paralysis of the abductors after novocaine-suprarenine spinal anesthesia. HERM. SCHUBERTS. *Klin. Monatsbl. Augenheilk.* 70, 151-6 (1923).

G. H. S.

Action of hexamethylenetetramine (particularly in meningitis) and the detection of formaldehyde in the urine, blood, and spinal fluid. WILLY H. CROHN. *Med. Klin.* 19, 654-7 (1923).—HCHO could not be detected in the blood, urine, or spinal fluid after the administration of urotropine.

G. H. S.

Effect of sodium chloride on the chemical changes in the blood of the dog after pyloric and intestinal obstructions. R. L. HADEN AND T. G. ORR. *J. Exptl. Med.* 38, 55-71 (1923); cf. C. A. 17, 9.—A fall in chlorides is the first and seemingly most significant change to take place in the blood after pyloric and intestinal obstruction, the chloride apparently being utilized by the body as a protective measure against the primary toxic substance. Expts. reported demonstrate that NaCl solns. have a marked effect in preventing and controlling the toxemia of pyloric and intestinal obstruction as shown in clinical symptoms and in chem. changes in the blood. Dogs given an abundant supply of distd. H_2O died more quickly than untreated control animals. Glucose solns. have no sp. value and $NaHCO_3$ solns. prolong life only a short while. Good therapeutic results have been obtained with very concd. solns. of NaCl as well as with dry NaCl given by mouth.

C. J. WEST

Entrance of convulsant dyes into the substance of the brain and spinal cord after an injury to these structures. H. C. SVZ. *J. Pharmacol.* 21, 263-90 (1923).—After injection of acid fuchsin into the dorsal sac of a frog and injury to the brain a marked absorption of the dye takes place followed by convulsions. The adsorbed dye appears to be uniformly distributed throughout the entire substance of the brain and cord and in the quantities employed it is always found to be present in these organs in the form of a colorless compd. The decolorized dye is found in the tissues 2 min. after brain injury, which is considered to be the cause for the increased adsorption of the dye. In frogs with intact cerebral nervous system one does not find adsorption or only to a very slight degree and these frogs rarely show convulsions. The acid fuchsin which comes into contact with the injured region, when blood contg. the dye bathes this area, does not enter to a marked degree the nerve substance at the injured place and does not spread out from there quickly into the other parts of brain and cord. The dye which is contained in the spinal fluid (after bleeding has occurred) appears not to be adsorbed by the substance of the central nervous system to any considerable extent. The meninges in frogs protect the brain against the influence of certain crystalloid and colloid

solns. brought into contact with their outside surface. 10% NaCl solns. of picrotoxin, strychnine nitrate and acid fuchsin put on the outside of these meninges cause convulsions only after the meninges have been cut open. Under these circumstances the acid fuchsin produces convulsions without brain injury because it is applied in high concn. Possible reasons for the above effect are discussed.

Effect of quinine intoxication on the respiratory center of the rabbit. H. SUGATA AND A. L. TATUM. *J. Pharmacol.* 21, 293-9(1923).—Quinine, in essentially toxic doses when administered to rabbits, causes a rise of alk. reserve capacity largely if not entirely due to diminution of pulmonary ventilation. This may occur, subsequent to proper dosage, in such an order as to cause retention of CO_2 without O_2 deficiency. In the intact animal respiratory vol. is decreased by the increased rate which is too shallow to be normally efficient. In double vagotomy alone, respiratory vol. is not essentially changed but with quinine it is increased above normal, leading to rapid fall in reserve and early death of the animal. Morphine, double vagotomy and quinine reduce respiratory vol. so that the reserve may not fall and the animal recovers from the acute effects of quinine. Quinine, therefore, appears to increase the irritability of the respiratory center: (a) reflex response to afferent vagus impulses—increasing rate at the expense of depth leading to under-ventilation; (b) in absence of vagal influences the increased irritability of the respiratory center to "hormone" action causes excessive or over-ventilation.

Distribution and elimination of organic arsenic compounds after intravenous administration. F. M. R. BULMER. *J. Pharmacol.* 21, 301-11(1923).—The salient features in the distribution of As are its high concn. in the liver very shortly after its injection; the rapid lowering of this concn. presumably by elimination of the As by the bile; the relatively large amt. in the lungs, especially after large doses and the maintenance of a high As content here, over a period of at least several days; and its retention by the long bones over a longer period than shown by any other tissue analyses. Only about 40% of the As administered can be accounted for in the urine and feces. More As is excreted in the feces than in the urine. The As is introduced to the feces by the bile. The liver rather than the kidney may thus be regarded as the As clearance depot.

Barbital narcosis and hypothermia in pigeons. M. M. ELLIS. *J. Pharmacol.* 21, 323-42(1923).—Intra-abdominal injections of barbital (I) produced in pigeons a definite series of changes in position and muscular activity, terminating in a fairly uniform and usually much prolonged narcosis. This narcosis lasted from 2 to 12 days in birds recovering and from 1 to 17 days in those receiving fatal doses. In general the duration of the narcosis varied with the amt. of barbital given below 300 mg. per kg. body wt. These injections of I also produced a rapid and pronounced lowering of the body temp. of pigeons, which averaged 0.8° during the 1st 15 mins., 1.7° during the 1st 30 min. and 2.8° during the 1st hr. The min. body temp. in the 1st stage was recorded about 2.5 hrs. after the injection of I and the depression averaged 3.8° at that time. The min. body temp. during the entire period of I narcosis appeared in the 1st 8 hrs. in over half the cases observed, but was delayed in some for 48 hrs. or more. Compared with control pigeons which were given neither food nor water for 12 days pigeons in I narcosis maintained a distinctly lower body temp. and lost wt. at a slightly lower wt. The min. fatal dose of I given intra-abdominally was between 225 and 250 mg. per kg. of body wt. for adult pigeons. Pigeons are more sensitive to I than cats, dogs, rabbits or frogs, although the depressions of body temp. produced in pigeons were not as great as those reported for some mammals. Satisfactory surgical anesthesia in pigeons was not obtained by the use of I alone.

Respiratory exchange and blood sugar curves of normal and diabetic subjects after adrenaline and insulin. R. S. LYMAN, ELIZABETH NICHOLLS AND WM. S. McCANN. *J. Pharmacol.* 21, 343-65(1923).—Subcutaneous adrenaline gave the usual rise of respiratory quotient (R. Q.), heat production and blood sugar, as well as the well known subjective and circulatory changes in both normal and diabetic individuals. The R. Q. of patients with diabetes did not reach as high a figure as in any control case. The patients formed 2 groups according as to whether the increment of heat production was above or below that of the normal subjects. No parallelism between the behavior of blood sugar after adrenaline and the severity of the disease could be made out. Insulin increased the R. Q. and heat production and greatly reduced the blood sugar in all expts. In some cases the R. Q. diminished slightly during the 1st 0.5 hr. after insulin. Pulse and blood pressure changes were slight and variable. Subjective symptoms were often more marked on the initial dose than on later injections irrespective of the level of blood sugar. Several normal persons had an extreme hypoglycemia without subjective sen-

sations. As diabetic patients improved clinically, the effect of the same dosage of insulin caused a more immediate but smaller drop in percentage of blood sugar and the sugar started to increase in a shorter time after the injection. Subjects who showed a slight reaction to adrenaline tended to give a relatively marked response to insulin. Injection of both insulin and adrenaline showed an antagonistic effect in their action on respiratory exchange, level of blood sugar and circulatory changes. The total result was the summation of the 2 factors.

C. J. WEST

Industrial medicine in Great Britain (LEGGE) 13. H_2S as an industrial poison (SAVERS, *et al.*) 13. Biological effects of Röntgen radiation from the rear of the anticathode (HALBERSTÄDTER) 3.

McNAIR, JAMES B.: *Rhus Dermatitis from Rhus toxicodendron, radicans and diversiloba (Poison Ivy): Its Pathology and Chemotherapy.* Chicago: University of Chicago Press. 298 pp. \$4. Reviewed in *J. Am. Med. Assoc.* 81, 683 (1923).

I—ZOOLOGY

R. A. GORTNER

Emulsin in the May bug. HERMANN BRUNSWIK. *Mikrokosmos*, 16, 163 7 (1923). May bugs were dissected and the various organs ground separately in amygdalin solns. in the presence of an antiseptic. The mixts. were allowed to stand in receptacles covered with watch glasses from which hung drops of 1% $AgNO_3$ soln. colored slightly with methylene blue. The presence of emulsin was shown by the formation of $AgCN$ crystals in the hanging drops. Emulsin was found in many of the organs and juices. Feeding tests with amygdalin showed the toxicity of HCN for the May bug to be very low.

JAMES A. BRADLEY

Localization of chemical and thermal sensitivity in paramécia and stentor. F. ALVERDES. *Zool. Anz.* 55, 19-21 (1922); *Physiol. Abstracts* 8, 54.—By chem. and thermal stimulation of pieces cut from *P. caudatum* and *S. polymorphus*, it is found that in the former sensitivity to both types of stimulus is practically completely limited to the mouth region, while in *Stentor* only the temperature perception, and not the chemical, is localized in the anterior end.

H. G.

Effect of some nutrients on the iodized tissues of some invertebrates of the larva of *Bufo vulgaris*. G. COTRONI. *Atti. accad. Lincei, Rend.* 30, 149-51 (1921); *Physiol. Abstracts* 8, 68.—Pieces of the musculature of *Squilla* and *Donax* were iodized by soaking in an aq. soln. contg. 29% KI and 1% I, washed and fed to the larvae of *Bufo vulgaris*. Metamorphosis was hastened, as with thyroid gland, or iodized vertebrate flesh. The experiments are regarded as preliminary.

H. G.

Crystals of hemoglobin of rodents, particularly of the hamster (German marmot). OTTO KRUMMACHER. *Z. Biol.* 77, 175-80 (1923).—Crystals of hemoglobin prep'd. from the blood of a hamster belong to the monoclinic system. Those obtained from most other mammals are rhombic, except those from the squirrel, which are hexagonal. Those from the pigeon are quadratic.

J. C. S.

Composition of the eggs during ovogenesis in the russet frog (*Rana fusca*). EMILE F. TERROINE AND H. BARTHELEMY. *Compt. rend.* 176, 1757-9 (1923); cf. C. A. 16, 971; 17, 1674.—Beginning just after the egg laying period the ovaries of 6 to 12 frogs were analyzed, the results of which are shown in the following table in which column I gives the dates, II the ratio of the wt. of the ovary to the total wt., III H_2O content, IV protein ($N \times 6.25$), V fat, VI cholesterol, VII sum total:

I	II	III	IV	V	VI	VII
Mar. 22-29	1.57	84.48	13.1	1.57	0.19	99.36
August 21	4.82	72.74	18.8	5.51	0.67	97.72
September 6-7	7.41	63.27	26.4	6.80	0.54	97.01
September 23	7.93	62.96	25.7	8.26	0.84	97.76
October 8-10	9.04	59.06	29.4	8.49	0.56	97.51
October 31 } November 2 }	10.49	56.86	32.1	9.20	0.71	98.87
November 28-9	12.40	55.91	30.9	9.54	0.47	96.82
December 31	11.67	65.32	30.7	9.13	0.64	96.71
February 10	12.58	58.12	29.8	8.59	0.54	97.05
March 1	15.00	59.3	27.9	10.30	0.62	98.72

These figures are discussed and a no. of new questions are raised.

L. W. RIGGS

Substances extracted from *Eledone moschata*. I. D. ACKERMANN, F. HOLTZ AND F. KUTSCHER. *Z. Biol.* 77, 241-4(1923).—Adenine and arginine have been isolated from the mussel, *Eledone moschata*. J. C. S.

The effect of food, starvation and low temperature on the catalase content of paramacia. W. E. BURGE. *Proc. Am. Physiol. Soc., Am. J. Physiol.* 63, 432(1923).—A temp. of 5° for 24 hrs. decreased the catalase of paramacia 38%. Starvation for 8 days decreased it 46%. The decrease in oxidation in paramacia brought about by low temps. and starvation is attributed to a decrease in catalase. J. F. LYMAN

12.—FOODS

W. D. BIGELOW AND A. E. STEVENSON

Report on arsenic in foods. R. M. HANN. *J. Assoc. Official Agr. Chem.* 7, 48-54 (1923); cf. *C. A.* 17, 1283.—The present report has, to some extent, reviewed the work of the previous referee, in an effort to summarize finally the results of the repeated collaborative study of the Gutzeit method. In addition, the KI reduction has been established as an essential step in the procedure. It has also been pointed out that HCl is now so generally employed that its use should be authorized in the methods of the Assoc. It is recommended (1) that the use of HCl be allowed as an alternative acid in the Gutzeit methods—20 cc. of 1 to 1 As-free HCl. (2) That the Gutzeit method for the detn. of As with the above revision and amendment be adopted as an official method. J. A. KENNEDY

Report on metals in foods. Tin. W. F. CLARKE. *J. Assoc. Official Agr. Chem.* 7, 46-7(1923); cf. *C. A.* 15, 903; 16, 1812; 17, 1511.—The Penniman method (zinc-iron pptn. method) in its present state is outlined. Further study is recommended. J. A. KENNEDY

The detection of pasteurized milk. W. D. FROST. *Wis. Univ. Studies Sci. No.* 2, 151-63(1921); *Exptl. Sta. Record* 48, 207.—The methylene blue stain method for the detection of pasteurized milk previously noted (*C. A.* 9, 1352) is described in greater detail, with colored illustrations to aid in the interpretation of the results. The tendency of the dye soln. to curdle the milk when used in the concn. originally recommended has been overcome by the use of a larger vol. of a more dil. soln. (1.5 g. in 1 l.). This is added to the milk vol. for vol. The mixt. is allowed to stand for 10 or 15 minutes, after which it is centrifuged at 2,000 r. p. m. for 10 minutes. The sediment is then smeared carefully on a glass slide without the use of water, and the slide is examed. first with a low power and finally with an oil immersion lens. In general the bacteria in the raw milk are stained, but in freshly pasteurized milk they are invisible. H. G.

Milk platelets and gel of rennet. E. HEKMA. *Arch. neerland. physiol.* 7, 223-6 (1922); *Physiol. Abstracts* 8, 76.—H. describes particles in milk which are retained by a Chamberland filter, and show Brownian movement, as "milk platelets," on analogy with blood platelets. They are probably composed of caseinogen or its Ca salt. In clotting with rennet in the presence of Ca, these "platelets" run together and form a network. In high dilutions of the milk they are seen to be joined together by the contractile threads, and are not in direct contact with each other. H. G.

Municipal milk control in Toronto. G. G. NASMITH AND R. GEORGE. *World's Health* 4, No. 6, 28-31(June, 1923). JACK J. HINMAN, JR.

Two simple methods for determining chlorine in milk. J. DROST. *Z. Nahr. Genussm.* 45, 246-53(1923).—Detn. of Cl in milk ash gives too low results since as high as 28% of the Cl may be lost in ashing. The following methods are accurate: (1). 25 g. of milk are weighed into a 250 cc. volumetric flask and 12.5 cc. of 5 N HNO₃ are added. After making up to vol. and shaking, the mixt. is allowed to stand, preferably overnight. It is then filtered and Cl detd. in 50 cc. of the filtrate by the Volhard method. (2). As a precipitant, 10 cc. of CuSO₄ soln. (Fehling's soln. No. 1) and 17.6 cc. of 0.25 N NaOH may be substituted for the HNO₃ used in the first method. D. B. DILL

Caviar, its composition, preservation and fermentation. G. HINARD. *Ann. fals.* 16, 324-32(1923).—H. gives a brief review of the compn. of caviar of different origins and also 8 analyses by himself showing: H₂O 48.26-52.72, crude proteins 24.88-29.50, crude fat 11.97-16.29, ash 3.85-6.81, N-free ext. 2.96-5.44, NaCl 2.27-5.29, NaCl-free ash 1.52-2.08, glycogenic carbohydrates 0.78-1.00%. A German pike caviar gave H₂O 78.31, crude proteins 11.50, crude fat 3.47, NaCl 4.57%. The best criterion of the state of preservation is the taste, and the most satisfactory chem. tests for indi-

cating it are acidity and N titratable with formaldehyde (via Sorensen) which give results agreeing with taste. Acidity should be detd. as follows: grind 20 g. thoroughly till all eggs are crushed and the membranes are disintegrated, add slowly, with const. stirring, first 50 cc. of distd. H₂O and then 50 cc. of 96% alc., transfer to a flask, stopper, shake thoroughly, let stand, filter; to a 25-cc. aliquot add 75 cc. of H₂O (to reduce the alc. content below 15%, as otherwise amines and NH₄ salts would react acid and interfere), and titrate with 0.1 N NaOH using phenolphthalein indicator. The N is detd. as usual by adding 10 cc. of CH₃O soln. and again titrating the acidity. The acidity of fresh and properly preserved caviar should be below 2 cc. of N NaOH per 100 g., and the N titratable with CH₃O should be below 0.050%. The flavor of caviar is due to a fermentative process affecting both proteins and fat (and possibly also carbohydrates). The fat is probably merely oxidized, while the proteins seem to undergo a slow diastic fermentation rather than a bacterial fermentation. Formic acid is the chief (and may be the only) volatile acid formed during fermentation, and gives the sharp taste to caviar. AcOH, butyric and valeric acids may also be present in much smaller amts.

A. P. C.

The limit of accuracy of the determination of water addition to meats. J. GROSS-FELD. *Z. Nahr. Genussm.* 45, 253-61 (1923).— Cf. C. A. 7, 3170; 16, 597, 3984. The results of Pannwitz and Harder (C. A. 17, 2020) are reviewed and new calens. are derived therefrom. It is concluded that Feder's method of detecting water addn. is sufficiently conservative and most reliable.

D. B. DILL

Reply to Dr. Seal and a few new observations on the water content of meats. E. FEDER. *Z. Nahr. Genussm.* 45, 261-79 (1923).— Cf. *Deut. Schlachthof-Ztg.* 23, 3 et seq. (1923). Chiefly polemical.

D. B. DILL

Feder's method for detecting water addition in sausage. E. JÜNGERMANN. *Z. Nahr. Genussm.* 45, 284-8 (1923).—Chiefly polemical.

D. B. DILL

Experimental data on pectin-sugar-acid gels. R. SUCHARIPA. *J. Assoc. Official Agr. Chem.* 7, 57-68 (1923).—Pectin-sucrose-acid gels may be prepd. in a cold way. Heat does not hasten the setting of such gels. Low temps. and evapn. are strong promoting factors. The formation of such gels is not a chem. reaction. It is the coagulation of pectin in the liquid sucrose-acid medium. Pectin is very slightly sol. in sucrose-acid solns. of certain concn. The mother liquor seps. even out of very tough jellies, though in a smaller amt. than out of soft jellies. The solid part left contains pectin only (after washing in alc.). The liquid part contains all the acid, sugar, traces of pectin, and a small amt. of CH₃OH. The methoxyl groups are split off in a small amt. only, since the recovered pectin forms good gels again with sugar and acid. Pectins with different methoxyl contents were prepd. Crude pectins differ from purified pectins not only by their ash content, but also by some org. compds. The differently methoxylated pectins form solns. of uneven viscosity. Two methods are described to compare gel-forming properties of various pectins. A device is described to serve as a gel-tester. Pectins will form gels increasing in strength with their increasing methoxyl content. Impurities in pectins have no effect on gel strength providing the same amt. of pectin is used. Long heating and high temp. and pressure destroy jelly power in pectins. A bibliography is appended.

J. A. KENNEDY

Artificial sweetening (saccharin) and its use in the fruit preservation industry. H. SERGER. *Chem.-Ztg.* 47, 98-100, 123-4, 145-6 (1923).—Various fruit products were sweetened with saccharin and subjected to sterilization and other operations incident to preservation. Several months later the canned goods were opened when it was found that products sweetened with saccharin alone are more watery and less satisfactory than those sweetened with sugar. The former products may be made more satisfactory by the addn. of strong sirup. Fruits preserved with a mixt. of saccharin and sugar were always sugar-like and of satisfactory taste and consistency. Saccharin sweetening is more lasting and more intense to the taste than sugar sweetening. This property is decreased instead of increased by the addn. of more sugar. At 100° saccharin is not decompd.; it appears neither to reduce the degree of sweetness nor to give rise to bitter decompn. products in noticeable amts. In marmalades, jellies and jams it was found that saccharin-sweetened products required the addn. of thickening agents such as agar or starch sirup. Over sweetening with saccharin gives a bitter taste, which, however, is overcome by the presence of fruit acids. In the presence of starch sirup and not too much saccharin the taste is always sugar-like and not obtrusive. Fruit juices to which saccharin was added were not changed in sweetness by pasteurization or by previous preservation with benzoate or HCOOH. Mother juice sweetened with saccharin has a greater fruit content than if sweetened with a sirup made of juice 7 to sugar 13.

L. W. RIGGS

Changes wrought in the grapefruit in the process of maturation. I. Natural changes. II. Factors affecting the composition of the fruit. F. A. LOPEZ. *J. Dept. Agr. Labor Porto Rico* 4, 103 pp.(1920); 5, 45(1921); *Expt. Sta. Record* 48, 329-30.—The changes that take place in the fruit during its development, such as increase in juice content, increase in weight, and decrease in the proportion and thickness of the skin, became less and less perceptible as maturity approaches. Obvious signs of maturity, such as color of the fruit, condition of the juice cells, taste of the juice, and general appearance, coincide with cessation in the increase of weight and juice and the decrease in the content of skin, as well as with the decrease in acid content and the increase of ratio of solids to acids; also with the end of the process of sugar elaboration and the beginning of inversion of sucrose. Taking the changes enumerated and the signs of maturity above referred to as criteria to judge the maturity of the fruit, it may be assumed that grapefruit in this region may not be considered ripe and fit to eat before the ratio of solids to acids in soln. in the juice has reached at least 7:1. This minimum ratio should be accompanied by the signs of maturity evident on inspection. The changes enumerated above apply in a general sense to the three varieties tested, but the rate at which they proceed and the extent to which they take place differ for each variety. Excessive rainfall causes delay in the process of maturation of grapefruit and increases the proportion of juice, but decreases that of solids and acids. The ratio of solids to acids is lower in rainy seasons than in seasons of moderate rainfall. The influence of soil type on the compn. and quality of the fruit is not very pronounced. The chem. compn. of the fruit does not greatly affect its quality, nor does the chem. compn. of the soil greatly affect that of the fruit. N is the only element of nutrition the amt. of which in the fruit may depend on the amt. present in the soil. However, the fertilizers used must be taken in consideration. Sweating has little effect on its compn., the most noticeable change being produced in the color. The most important changes undergone by grapefruit in storage are loss in weight and inversion of sucrose. H. G.

The occurrence of a hesperidin precipitate in oranges. C. GRIEBEL. *Z. Nahr. Genussm.* 45, 238-40(1923).—Typical hesperidin crystals were found in the endocarp of oranges which were in a state of incipient decay. D. B. DILL

Coloring Satsuma oranges in Alabama. R. C. WRIGHT. U. S. Dept. Agr., *Bull.* 1159, 1-22(1923).—Satsuma oranges which become suitable for food some weeks before they assume a yellow color on the tree may be colored by the action of the exhaust gas given off by a gasoline engine or by the incomplete combustion of kerosene in a stove. This gas destroys the green chlorophyll which masks the yellow color. Fruit carrying up to 40% natural ripe color will ordinarily require an exposure of 4 days to develop a full yellow color. W. H. ROSS

Histology and chemistry of the avocado. W. J. STONEBACK AND RALPH CALVERT. *Am. J. Pharm.* 95, 598-612(1923).—The proportions of the chem. constituents change in each variety according to the degree of the maturity of the fruits. Variation is particularly noticeable in regard to the fat content. Up to a certain point, the fat content increases with the maturity of the fruit. The total dry matter in the edible portion is greater than that in any other fresh fruit, the one nearest approaching it being the banana, which contains 25%. The avocado contains an av. of 30%. The protein content, which averages 2%, is higher than that of any other fresh fruit. The % of carbohydrates is not high compared with many fruits, because the avocado contains almost no sugar. The amt. of mineral matter is much greater than that in other fresh fruits. Salts of Na, K, Mg, and Ca compose more than $\frac{1}{4}$ of the ash. This fact places the avocado among the foods which yield an excess of the base-forming elements, as opposed to nuts, which furnish an excess of acid-forming elements. The chief value of the avocado as a food is due to its high % of fat (av. 20%). The caloric or energy-producing value of the avocado is very high. One lb. of the edible portion represents an av. of 1000 cal. The max. yield is nearly twice that of av. lean meat. The Collins, a Guatemalan variety investigated, shows along with general characteristics, the following analysis: moisture 66%, protein 1.21%, fat 25.26%, carbohydrates 6.44%, ash 1.09%, immersion refractometer reading of juice 62.8. W. G. GAESSLER

The iron content of lettuce. AARON LICHTIN. *Am. J. Pharm.* 95, 154-9(1923).—The av. Fe content of the lettuce examd. was 0.00213% as detd. by the following method. The edible portions of the heads were washed and desiccated in a drying oven to const. wt. at a temp. varying from 95° to 97°. Care was taken to avoid contact with metallic surfaces. The dried material was comminuted and incinerated in a silica dish, protected from dust and air currents. The resulting ash was then weighed and stored in glass-stoppered bottles. A quantity of ash was carefully weighed in a

tared Erlenmeyer flask, and measured quantities of strong H_2SO_4 (95.6%) and distd. water were added; the mixt. was kept boiling for 1 hr. and, after cooling, filtered and the filters were washed with distd. water to make the filtrate measure either 75 or 100 cc. A standard Fe soln. was prepd. by dissolving 0.21 g. of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 50 cc. distd. H_2O and 7.5 cc. 20% H_2SO_4 , then oxidizing the ferrous salt with 0.1 *N* K_2MnO_4 soln. and dilg. to 300 cc. Each cc. of this standard soln. contains 0.0001 g. of Fe. Three color standards were prepd. by mixing for *A* 10 cc., for *B* 1 cc. and for *C* 0.2 cc. of the standard Fe soln. with 10 cc. *N* KCNS soln. and then dilg. to 100 cc. with 10% H_2SO_4 . Therefore, color standard *A* contains 0.001 g. of Fe in 100 cc. of soln., *B* 0.0001 g., and *C* 0.00002 g. A portion of the acid extn. of the ash was placed in a buret graduated to 0.1 cc. and allowed to drop into a Nessler jar contg. 10 cc. H_2SO_4 (iron-free), 10 cc. KCNS and water to make about 90 cc. The color soln., which was formed by the dropping of the liquid from the buret, was compared and matched with 100 cc. of the nearest color standard (*A*, *B* or *C*). The quantity of the liquid dropped was noted and the quantity of Fe in the acid extn. calcd. according to this formula: (g. Fe in color standard \times cc. total acid extn.) / cc. acid extn. used in expt. = g. Fe in acid extn.

W. G. GAESSLER

High solanine content in potatoes. A. BÖMER and H. MATTIS. *Z. Nahr. Genussm.* 45, 288-91 (1923).—Several cases of poisoning from eating potatoes of abnormally high solanine content are reported. The following procedure for detg. solanine is suggested: A 200 g. sample from several cleaned potatoes is grated and washed into a flask with about 250 cc. of water. The mixt. is allowed to stand at room temp. for some time, with occasional shaking. It is then transferred to a linen bag in a fruit press and pressed thoroughly. The operation is repeated 3 times with 250 cc. of water, about 5 drops of AcOH and with digestion for 30 min. at room temp. each time. The united press liquor is made weakly alk. with NH_4OH . It is transferred to a glazed porcelain dish together with about 10 g. of kieselguhr and evapd. to dryness. Occasional stirring and washing down with warm water are necessary during evapn. The completely dried residue is ground to a powder and extd. 5 hrs. in a Soxhlet app. with 95% alc. After powdering the residue it is again extd. with alc. as before. The residue is freed from alc. and is dissolved in water weakly acidified with AcOH . The soln. is made alk. with NH_4OH and warmed for a short time on the water bath. The pptd. solanine is filtered and washed with 2.5% NH_4OH . It is dissolved in alc., the soln. filtered the alc. distd. off and the residue is dissolved and pptd. as before. The colorless solanine ppt. is collected on a tared filter, dried and weighed. Normal potatoes showed 2.0 to 7.5 mg. of solanine per 100 g. Abnormal potatoes contained 26.1 to 58.8 mg. per 100 g.

D. B. DILL

Deterioration of mushrooms on extraction with water and rejection of the extract. T. SABALITSCHKA and H. RIESENBERG. *Ber. pharm. Ges.* 33, 12-4 (1923).—Expts. were made to det. the amt. and nature of the sol. matter extd. from the edible fungi, *Boletus edulis* and *Tricholoma equestre*, by boiling H_2O . The fungi contained 14.8 and 15.7% of dry substance, resp., and of this 6.7 and 6.9% were extd., representing a loss of 45 and 44%. Of the total nitrogenous matter, amounting to 5.22 and 1.63%, resp., calcd. on the fresh fungi, no less than 50% was removed by the boiling H_2O in the former case and 29% in the latter. It is therefore undesirable, when prepg. the fungi for food purposes to boil them in H_2O , and then reject the ext., as much valuable food material is thereby lost. The idea that boiling in H_2O removes poisonous substances is erroneous, except in the case of various species of *Lactaria* and the *Helvella esculenta*.

J. S. C. I.

A preliminary report on the presence of primary amines in canned mushrooms. C. F. JABLONSKI. *J. Assoc. Official Agr. Chem.* 7, 45-6 (1923).—In the course of examn. of canned mushrooms for added coloring matter it was noted that the yellow supernatant liquid behaved like most vegetable coloring matters, viz., no appreciable dyeing on wool or cotton; no distinct actions of acids or alkalis, save that of increasing or decreasing the tint a slight amt.; no action with SnCl_2 or other reducing agents; and no stripping or redyeing. However, when a portion of the original liquid was acidified with HCl , diazotized, and coupled with an alk. soln. of α -naphthol an orange-red color was obtained. Like results were obtained with the yellow color extd. from drained mushrooms; also from several other brands of bleached and unbleached mushrooms. The orange-red color was sepd. into 2 component colors, one ether-sol. and the other H_2O -sol. A piece of wool dyed in this orange-colored H_2O soln. gave reactions similar to Orange I, S. & J. No. 85. From this it would appear that a small amt. of aniline or sulfanilic acid or both is present in canned mushrooms. Bleached mushrooms gave a greater amt. of H_2O -sol. dye and a proportionally smaller amt. of ether-sol. dye.

The reverse was noted with unbleached mushrooms. Additional investigation is being made.

The occurrence of spherical tyrosine crystals in bean meal. J. A. KENNEDY. *C. GRIEBEL. Z. Nahr. Genussm.* 45, 237-8(1923).—Spherical tyrosine crystals were found in beetle-infested beans and bean flour. These crystals are characteristic constituents of the excreta of the seed beetle (*Larva pallidicornis* Boh.). D. B. DILL.

Determination of lipoids and lipid-phosphoric acid in flours, alimentary pastes, noodles and eggs. RAYMOND HERTWIG. *J. Assoc. Official Agr. Chem.* 7, 91-8(1923).—(A). As adapted to *alimentary pastes, noodles, and flours*: Grind the sample to pass an 80-mesh sieve. Place 10 g. of sample and 30 cc. of 70% alc. in a 200 cc. nursing bottle and set in a H₂O bath kept at 75-80°. Give the bottle a gentle rotary motion so as to moisten all of the particles with the alc. Heat for 15 min. with frequent mixings by the same rotary motion. Add 55 cc. of 95% alc., stopper the bottle, and shake vigorously for 2 min. Add 85 cc. of ether, dried over Na, and shake well for 5 min. The sample should now be in a fine state of division. Centrifuge just sufficiently to pack the sample lightly. Decant the liquid into a 250 cc. beaker contg. some bits of broken porcelain, rinsing off the bottle neck with ether. Repeat the extn. of the sample with 3 successive 25 cc. portions of ether satd. with H₂O, shaking 1 or 2 mins. each time, centrifuging, and decanting into the beaker contg. the first ext. If the sample packs too firmly after centrifuging, loosen it with a glass rod; should it become too dry to pack sufficiently to permit easy decantation, add a few drops of H₂O to the ether. Evap. the combined ether-alc. ext. to dryness on the steam bath; if necessary hasten the evapn. of the last drops of H₂O by adding a little abs. alc. Dry the lipoids thus obtained in an oven at 100° for 45 min. Dissolve the dry lipoids in about 15 cc. of CHCl₃ and filter. For this filtration the following app. is recommended: In the top of a bell jar connected with a filter pump place the inner tube of a Knorr fat extn. app. (E. and A. No. 2810, 1920 catalog) contg. an asbestos pad which has been washed with alc. and ether and dried. (The form of tube with a removable disk is preferred.) Filter the CHCl₃ soln. through this pad, receiving the filtrate in a weighed Pt dish. Carefully remove all traces of lipoids from the beaker by means of a CHCl₃ wash bottle. The filtrate should be perfectly clear. Should the asbestos become clogged, hasten the filtration by gently rubbing the surface of the pad with a glass rod. Evap. the CHCl₃ off on the steam bath and dry to a const. wt. in the H₂O oven (approx. 75 min.). Report as lipoids. Saponify by warming with 5-10 cc. of 4% alc. KOH, evap. to dryness, and char well in a furnace below red heat. Ext. with HNO₃ and det. H₃PO₄ by the official volumetric method, and report as lipid H₃PO₄. (B). As adapted to *dried powd. eggs*. Use the filtering app. recommended in the preceding method for the filtration of the CHCl₃ soln. Place 3 g. of the dry egg product in the Knorr extn. tube with an asbestos pad and wash with ether until most of the fat is removed. Stir the sample with a glass rod during this operation. Collect the filtrate in a 250 cc. beaker. Evap. the ether on the steam bath. By means of a wire, force the egg residue and asbestos pad, as one mass, out of the extn. tube into a small glass mortar. Carefully wash from the tube, and especially the tip, any adhering fat and add it to the main ethereal soln. Allow the ether in the egg residue to evap. spontaneously. Add 2-3 g. of finely powd. CaCO₃ and rub to a fine powder with a glass pestle (to prevent lumping after treatment with 70% alc.). Transfer the mixt. to a 200 cc. nursing bottle. Rinse the mortar and pestle with ether and add to the ethereal fat soln. Add 20 cc. of 70% alc. and place in a H₂O bath at 75° to 80°. Heat for 15 min., shaking frequently with a rotary motion. Add 35 cc. of 95% alc. and shake 2 min. Add 55 cc. of dry ether and shake 5 min. Centrifuge and decant the alc.-ether into the beaker contg. the ether ext. Wash the egg residue with three 15-cc. portions of ether satd. with H₂O. Dry the lipoids thus obtained for 1 hr. in an H₂O oven. Take up the dry lipoids in CHCl₃ and filter into a Pt dish as indicated in A. Evap. off the CHCl₃ and dry to const. wt. in a H₂O oven (approx. 75 min.). Report as lipoids. Det. the lipid-H₃PO₄ according to A. The official gravimetric method in preference to the volumetric method is recommended for this detn. because of the large quantity of H₃PO₄. (C). As adapted to *liquid eggs*. Mix sample with an egg beater and weigh out 10 g. into a 200 cc. nursing bottle; add 100 cc. of ether and shake the mixt. well. Add five 5 cc. portions of 95% alc., shaking after each addn. The gradual addn. of alc. with shaking coagulates the protein in a very fine state. Centrifuge lightly and pour the ether-alc. soln. off into a 250 cc. beaker. Place on a steam bath. Shake the residue in the bottle free by a rotary motion with 25 cc. of 70% alc. and place in a H₂O bath at 75° to 80° for 15 min. Shake the mixt. frequently with a rotary motion. Add 46 cc. of 95% alc. and shake 2 min. Add 70 cc. of dry ether and shake

5 min. From here the procedure is the same as that for dried eggs, given in B. "Centrifuge and decant the alc. ether," etc. The method yields results markedly higher in general than are those obtained by other available methods. Recovery of lipid- H_2PO_4 from a noodle over 1 yr. old was 81% of theory, and from a freshly made noodle, 89%. Expt. showed that a ground noodle, exposed to moisture-satd. air at room temp., fell off rather rapidly in lipid- H_2PO_4 content. Noodles are exposed to similar conditions during manuf. The recovery of less than the theoretical content of lipid- H_2PO_4 from a noodle by the method is very probably due to partial decompn. of the lipins during the mixing and drying of the noodle. In case, the egg solids in a noodle from its lipid- H_2PO_4 content, allowance should be made for the loss during its manuf. of some of the lipid- H_2PO_4 of the ingredients. It is suggested that the lipid- H_2PO_4 of the noodle be multiplied by 1.1 before making this calcn. The alc. ether ext. detd. by neutral extn. method contains many substances besides neutral fat. The term lipid is used to designate these in order to distinguish them from those of the ordinary ether extn. The H_2PO_4 of the ext. is termed lipid- H_2PO_4 . J. A. KENNEDY

Analytical data on French honeys. C. F. MUTTELET AND (MISS) J. MOROV. *Ann. fals.* 16, 344-51(1923).—Analyses of 46 samples are tabulated and commented on. Attention is drawn to the possibility of very low levo-rotation and even dextro-rotation with honeys produced from coniferae, which also contain appreciable amts. of dextrans. Sucrose can go as high as 12% in insufficiently matured honeys, but seldom exceeds 6%. Acidity as formic acids is 0.038-0.142%. Fiehe's reaction for furfural was negative even in honeys which had been heated during extn. A. P.-C.

New simple method for the determination of albuminoids in honey. O. LAXA. *Ann. fals.* 16, 286-9(1923).—To 8 g. of honey in a 150-cc. Soxhlet extn. flask add 4 cc. of water, dissolve with heat, add 100 cc. of 96% alc., stopper, let stand overnight, carefully decant the clear soln. (if the ppt. does not adhere to the glass, filter through a tared filter), wash with 10 cc. of alc., dry the flask at 100° for 2 hrs., dissolve the dextrans and sugars in cold water, dry the residue at 100°, and weigh. This gives true albuminoids, but not necessarily all the nitrogenous substances. A. P.-C.

Production of sirup from sweet potatoes. H. C. GORE, H. C. REESE AND J. O. REED. U. S. Dept. Agr., *Bull.* 1153, 1-33(1923).—A detailed account is given of a method that has been developed for the com. manuf. of sirup from sweet potatoes. Conversion of starch is accomplished satisfactorily by using malt equiv. to 0.2% of the wt. of the potatoes, by maintaining a temp. of 140° F. and by allowing the sirup to stand for 45 min. after the addition of the malt. Satisfactory results were obtained in the filtration of the sirup by using ignited kieselguhr. An av. yield of 1.46 gals. of sirup to a 50-lb. bushel of potatoes was obtained over a period of 2 seasons. W. H. ROSS

Report on non-alcoholic beverages and flavoring extracts. W. W. SKINNER. *J. Assoc. Official Agr. Chem.* 7, 39-41(1923).—Mention is made and references are given of a few articles of an analytical nature which have appeared in the past 2 yrs. It is recommended: (1) That as the subjects of non-alc. beverages and of flavoring exts. are closely allied they be combined under one subject, such as "beverage and household flavors and non-alc. beverages." The term "flavor" is preferred to the term "flavoring ext.," since from the standpoint of the enforcement of the Federal Food and Drugs Act the two terms are not synonymous. The term "flavor" is considered to be much broader, and the term "flavoring ext." to be limited to those flavors which have a menstruum of C_2H_5OH of proper strength. (2) That the referee for next yr. give consideration to methods of analysis for non-alc. flavors such as, for example, detn. of the quantity of orange oil in peanut oil and in mineral oil. J. A. K.

Halawa (Oriental almond-cake). A. AZADIAN. *Ann. fals.* 16, 289-92(1923).—"Halawa" is prepd. from sugar and ground nuts or ground sesame seeds ("tahinya"), and is a current article of diet among the poorer classes of Egyptians. Analysis of 12 samples shows: sugar 9.0-54.4, oil 20.9-28.0%. A. PAPINEAU-COUTURE

Composition of commercial mustard seeds and the detection of added mustard bran in prepared mustard. RAYMOND HERTWIG. *J. Assoc. Official Agr. Chem.* 7, 68-83(1923).—Three distinct objects were in view: (1) to det. the general compn. and in particular the crude fiber content of com. mustard seeds as used at present by manufacturers of prepd. mustard; (2) to ascertain whether the proposed modified method for the detn. of crude fiber in prepd. mustard gives results which are comparable to the crude fiber content of the original seed used in the manuf. of the product; and (3) to develop any additional means of detecting small proportions of added mustard bran in prepd. mustard. Methods of analysis (A. O. A. C. except for few changes); 5 pages of tabulated analytical data; comparison of moisture detns. in water oven, air

oven, and vacuum oven; and discussion of data are given. Conclusions: (1) Analyses are given of 43 com. mustard seeds. For comparison there are included 3 mustard brans, 1 mustard flour, 2 prepd. mustards of known compn., and 15 com. prepd. mustards. (2) Coarsely ground seed yields a slightly lower ether ext. than finely ground seed. (3) Degree of fineness of division of mustard seed affects the crude fiber detn. Defatted seed ground in a mortar with a pestle shows a crude fiber content similar to that of the same seed made into a prepd. mustard by the usual com. process. (4) The analyses of 2 prepd. mustards of known compn. did not differ notably from the analyses of their respective seeds. The addn. of spices to seeds, in amts. as used in prepd. mustard, modifies only slightly the compn. of the final product. (5) The mustard seeds analyzed are all quite uniform in their compn. Ratios between certain constituents are also quite uniform. The compn. of mustard bran and the ratios between certain constituents differ greatly from those of mustard seed. These differences offer a means of detecting added bran in prepd. mustards. (6) The N and crude fiber content of a prepd. mustard alone is sufficient to detect adulteration with mustard bran in some cases. Certain ratios between the N, crude fiber, total H_2PO_4 , CaO, and MgO will often indicate the presence of added bran even when the crude fiber is not excessive. (7) With prepd. mustards suspected of contg. added bran, detns. should be made for solids, N, crude fiber (Hilts-Hertwig), ether ext., acid-insol. ash, Cl as NaCl, total H_2PO_4 (by method described), CaO, and MgO. A microscopical exam. should also be made. J. A. KENNEDY

Indian condiments. HANNS FISCHER. *Chem.-Ztg.* 47, 665-6(1923).—General descriptions are given of the culture, prepn. and use in India of betelpepper, betelnut, tobacco, opium and hashish. L. W. RIGGS

The reducing power of some volatile oils and the adaptation thereof to the evaluation of cloves. P. N. VAN ECK. *Pharm. Weekblad* 60, 905-10(1923).—Eugenol readily reduces salts of Ag, Au, and cupric Cu, but not $HgCl_2$, Nylander's reagent or Eder's reagent ($HgCl_2 + (NH_4)_2C_2O_4$). Ferric salts are reduced to ferrous and the latter in the presence of $K_3Fe(CN)_6$ forms Prussian blue. The proposed quant. method is based upon this last reaction. Place 250 mg. of powd. cloves and 25 cc. of H_2O in a 250 cc. wide mouth flask and distil with steam until 150-175 cc. of distillate have been collected. Make up the vol. to 200 cc. Transfer a 100 cc. aliquot to a colorimeter glass and add 25 drops of a mixt. of equal parts of 0.074% $FeCl_3$ soln. and 0.1% $K_3Fe(CN)_6$ soln. In a 2nd colorimeter glass place 100 cc. of a eugenol soln. contg. 20 mg. per 100 cc., and add 25 drops of the above reagent. Let stand 15 min. and compare the colors by means of a colorimeter. Good cloves contain up to 20% oil, of which 80% is eugenol. If, for example, the color of the test reaction = $\frac{1}{4}$ that of the standard, the oil content of the sample is 15%. A. W. DOX

Experimental researches on the factors which determine in legumes resistance to cooking and on the agents used to modify it. A. DE DOMINICIS. *Ann. scuola agr. Portici* [2] 16, 31 pp.(1920).—Expts. show that, as regards boiling, the hardness of legumes (kidney beans, chick peas and beans) depends on their resistance to the penetration of H_2O . The greater the quantity of H_2O that can be absorbed, the more easily a seed cooks and the greater the quantity of H_2O actually absorbed the more the seed is cooked. All the chem. and phys. processes occurring in cooking are related to the proportion of absorbed H_2O . The resistance of seeds to absorption of H_2O is not due to presupposed impermeable mineral deposits composed of insol. Ca compds. because the resistance is overcome by alkalis but not by acids, which ought to attack the carbonate or silicate of Ca more energetically than do alkalis. Acids, on the contrary, intensify the resistance. Oxalic acid does so less than H_2SO_4 and HCl, notwithstanding its property of rendering Ca insol. The resistance cannot be related to the compactness of the integuments because, if alkalis reduced it by rendering certain elements sol., acids ought either to act similarly or remain without action and ought not in any case to increase it. Nor can it be related to the action of the ordinary ion of hard waters on insol. Ca compds., because (1) hard seeds resist the action of soft H_2O also and the hypothesis of the existence of these mineral formations has already been disproved; (2) salts other than Ca salts and even acids exert the same effect. The hypothesis of the formation of insol. Ca compds. by the cooking itself is untenable for the same reasons. The resistance cannot be associated with excessive quantities of wax or other fatty material, possibly existing in the cuticle of the seeds, because it does not yield to treatment with alc. and ether. Electrolytes penetrate into the seeds in different proportions than those in which they occur in the sols; alkalis and acids in greater proportions, salts in smaller proportions. Their penetration into seeds is therefore not the result of a simple process of diffusion, however one may wish to in-

interpret the properties constituting the permeability of plant membranes. The variations which the %s of electrolyte incorporated by the seeds undergo with concn. of the solns. correspond, on the contrary, to a fundamental law of adsorption by solid and colloidal adsorbents; viz., the coeff. of adsorption is not const. but increases with diminution of the concn. The substance that constitutes the seeds and exerts the adsorbent power towards electrolytes belongs to those colloidal forms which arise by concn. of the dispersive medium and present the property of restoring it in a measure corresponding to their degree of reversibility. The phenomenon of the swelling of the seeds in the presence of H_2O consists consequently of a process of imbibition, as is shown by the contraction in vol. with respect to the sum of the vols. of the seed and the absorbed H_2O , the development of heat at the moment of absorption, the optical phenomena that accompany it, the selective power towards liquids, the rapidity of the process and especially the influence of electrolytes. The action that the integuments and membranes may exert is secondary and indirect. The degree of reversibility of these colloidal forms is connected with the conditions of the medium in which their formation takes place and corresponds to the degree of their affinity for H_2O . ALBERT R. MERZ

The use of ligneous materials for the feeding of cattle. III. F. SCURTI AND G. DROGOU. *Staz. sper. agrar. ital.* 55, 13-23(1922); cf. *C. A.* 14, 3732; 15, 3532.—Grape vine branches and decorticated hemp stalks, ground and dried at 100° , analyze 0.64, 0.85% fat (ether ext.); 7.17, 4.71% crude protein; 21.66, 36.44% cellulose; 3.18, 1.62% ash; 67.34, 56.39% non-nitrogenous ext. and 24.0, 29.45% pentosans, resp. These substances were treated with H_2SO_4 , HCl and HNO_3 under pressure, the proportions of sol. and insol. portions detd. and the insol. portion was analyzed. Such treatment with mineral acids gave 71.58, 68.06% cellulosic pulp and 31.20, 27.9% sugar compds., resp. The results show the possibility and the advantage of these ligneous materials, which have so far had no other use than as fuel, being converted into products that are excellent feed for cattle. IV. F. SCURTI AND V. VEZZANI. *Ibid.* 24-8.—Cellulosic pulps, prepd. from corn cobs and wheat straw, were fed to cows, swine, rabbits and chickens. Cellulosic pulp cake gives excellent results as a substitute for more costly and possibly less efficient products in the feeding of cattle. The commencement of the use of this feed requires a little care but the results justify the best hopes for the future and encourage the carrying out of systematic feeding tests on different animals. ALBERT R. MERZ

The content of the rumen for the feeding of cattle. CESARE D'ALPONSO. *Ann. scuola agr. Portici* [2] 16, 1-14(1920).—The content of the rumen of bovine animals weighs 25-45 kg. An analysis of a sun-dried sample gave H_2O 12.42%, crude protein 10.38%, crude fat 1.70%, cellulose 22.24%, pure protein 9.24%, ash 16.28%, digestible protein (artificial digestion) 6.12% and N-free ext. 37.08%. Sun-drying appears the best, simplest, most practical method for its treatment as compared with Col. Aruch's method of washing and sun-drying and his method of drying by pressure and that of oven-drying. Feeding expts. lead to the following conclusions: (1) The content of the rumen is not injurious to the health of animals to which it is fed. (2) Because of its slightly disagreeable odor which persists on drying it is eaten by animals only when substituted for other food in suitable proportion. (3) It harms neither the live wt. of chickens nor the production of eggs. (4) It exerts no harmful influence on the increase of live wt. of young swine to which it is fed in place of bran. (5) Given the ease of prepn., the quantity which can be had at individual slaughter-houses, the not negligible nutritive value, and the low cost at which it can be acquired, it permits the realization of an economic advantage much greater than that ordinarily obtained by using it as fertilizer. ALBERT R. MERZ

Greasewood as a poisonous plant (MARSH, *et al.*) 11D. Effect of $HCHO$ upon the vitamin content of milk (BLEHLE, SEYMOUR) 11E. Caffeine and sodium benzoate (ROSIN) 17. The vitamin hypothesis and its practical significance in stock feeding (ORR) 11E.

GROSSFELD, J.: Tabelle und Anleitung zur Ermittlung des Fettgehaltes nach Vereinfachtem Verfahren in Nahrungsmitteln, Futtermitteln und Gebrauchsgegenständen. Berlin: J. Springer. 12 pp. 1s.

13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

- The aim and function of the chemical engineer. W. H. COLEMAN. *Chem. Age* (London) 9, 197-8(1923). E. H.
- Transport facilities in chemical works. HERBERT BLYTH. *Chem. Age* (London) 9, 192-4(1923).—The works of the United Alkali Co. at Widner is described. E. H.
- Chemical industries in Sweden during fifty years. ANON. *Medd. Sveriges Kem. Ind.* 6, 83-94(1923).—An economic review based on official figures. A. R. ROSE
- General notes on crushing and grinding. B. W. ROGERS. *Chem. Met. Eng.* 29, 432-4(1923). Pulverizing. HARLOWE HARDINGE. *Ibid* 434-6. Pebble or ball mills for mixing and grinding. H. F. KLEINFELDT. *Ibid* 436-8. Chipping wood for chemical pulp. *Ibid* 438. Disintegration of wood for mechanical pulp. J. J. CASE. *Ibid* 439-40. Secondary crushing of talc. ANON. *Ibid* 440. Equipment used for agitating and stirring. C. H. TYLER. *Ibid* 441-4. Mixing and kneading with machinery. H. B. VOLLRATH. *Ibid* 444-5. Principles and practice for separation of solids from one another. C. E. LOCKE. *Ibid* 446-8. Centrifugal separation of solids from solids in air. R. M. GAY. *Ibid* 448-50. Pulp screening—solids from solids separation in solution. R. B. WOLF. *Ibid* 450-1. Theory and practice of thickening. L. H. TYLER. *Ibid* 452-4. Progress and technic of filtration. ARTHUR WRIGHT. *Ibid* 455-7. The filter press in filtration. M. J. SAYLES. *Ibid* 457-8. Is there a centrifugal solution for your production problem? L. H. CLARK. *Ibid* 459-64. A new field for the centrifuge? O. C. RALSTON. *Ibid* 464. Surveying the possibilities in mechanical gas-solids separation. M. I. DORFAN. *Ibid* 465-7. Recovery of fine solids from air and gases by suction filters. F. LAJORGENSEN. *Ibid* 467-70. Fundamentals of gravity leaching. A. W. ALLEN. *Ibid* 471-2. Diffusion process in beet-sugar industry. R. W. SHAFOR. *Ibid* 472-4. Modern types of evaporators. W. L. BADGER. *Ibid* 475-8. Solving the evaporation problems of the soap industry. W. E. SANGER. *Ibid* 478-81. Fractional distillation. E. J. WINTER. *Ibid* 482-4. Recovering values from waste products by distillation. HENRY ARNSTEIN. *Ibid* 485-7. Applications of drying equipment. L. R. CHRISTIE. *Ibid* 488-90. Drying at atmospheric pressure through use of fans. J. M. MATTHEWS. *Ibid* 490-2. Vacuum drying. GRAHAM DEVINE. *Ibid* 492-4. Crystallization. G. T. WALKER. *Ibid* 495-8. Vacuum-pan evaporation in the sugar industry. C. F. HUTTLINGER. *Ibid* 498-9. Basic principles underlying gas absorption. E. M. BAKER. *Ibid* 500-2. How Norsk Hydro absorbs its dilute nitrous gases. T. G. HAGEMANN. *Ibid* 502-3. Tower fillings for industrial absorption. P. D. V. MANNING. *Ibid* 504-5. Refrigeration: what it is and how to use it. S. A. WOOLNER. *Ibid* 506-11.—This entire no. of *Chem. Met. Eng.* is devoted to a symposium on "unit processes." E. H.
- Industrial adsorption of gas and vapor with activated carbon. A. B. RAY. *Chem. Met. Eng.* 29, 354-9(1923).—An efficient activated C must possess mech. strength and a relatively high apparent d. Activated C possesses a sp. attraction for the vapors of numerous solvents. Even when dripping with water it will strip natural gas of gasoline. Silica gel possesses a sp. attraction for water vapor, and will adsorb the usual solvent vapors only after it has been thoroughly dried. In addn. to solvent vapor recovery and manuf. of gasoline from natural gas, activated C is adapted to the purification of coal gas, C_2H_2 , CO_2 , NH_3 , H_2 , etc. It is of use in the storage of compressed gases, for obtaining high vacua and in catalytic reactions. A very good bibliography is appended. E. G. R. ARDAGH
- Organic extraction and absorption medium. G. SCHMITT. *Wissensch. und Ind.* 1, 8-10(1922).—A soln. of SO_2 in acetone readily dissolves unsatd. org. compds. and resins, and can be used for extg. coal, lignite, peat, etc., for the selective extn. of solid or liquid mixts. of hydrocarbons, for refining oils, and for absorbing gaseous olefinic hydrocarbons. The soln. can be recovered from extd. material by distn. and has the advantage over liquid SO_2 in that cooling below 0° is not necessary for its use. J. S. C. I.
- Evaporation by means of thermocompression. LEONE LEVI BIANCHINI. *Giorn. chim. ind. applicata* 5, 219-25(1922).—Discussion of the theory and practice of evapn. by thermocompression. B. applies it specifically to the following cases: (a) concn. of soda washings from causticizing process, up to b. p. $108-110^\circ$; (b) concn. of sulfite lixiviations; (c) production of distd. H_2O and evapn. of org. liquids; (d) evapn. of electrolytic solns. Thermocompression is of particular utility in countries poor in fuel, while for low boiling liquids it has advantages even where steam costs little.

ROBERT S. FOSMONTIER

A short-cut interpretation of drying data. A. F. RANDOLPH. *Chem. Met. Eng.* **29**, 62(1923).—Certain drying expts. indicated that the rate of loss of solvent was proportional to the amt. of solvent present in the material above a limiting amt. not removable. This gives an equation of the form $s = be^{-kt} + a$, where s is the amt. of solvent present, t the time, a the final amt. not removable, b a const. depending on the solvent, and k a const. depending on the thickness of the material. On semi-logarithmic paper this equation gives a curve, but if it were not for the const. a , it would be a straight line. Plot the equation on semi-log paper without the term $(-a)$, then re-label the ordinates by adding $-a$.

W. L. BADGER

Steam-turbine-driven centrifugals. V. DINTR. *Z. Zuckerind. czechoslov. Rep.* **47**, 444-7(1923).—Tests were made on an exptl. model from Breitfeld, Danek & Co. With steam at 90 lbs. gage and exhaust at 9 lbs., as it took from 2.5 to 3.5 min. to come up to speed, the steam consumption per min. dropped from 15 kg. to 9 kg. per min. Lowering the steam pressure increased the steam consumption, but raising it above 90 lbs. decreased it very little. About 1.75 kg. steam per min. was used during running. The thermal efficiency of the turbine is low, so that the exhaust is somewhat superheated. Making certain assumption as to the efficiency of other power devices, it is calcd. that the mech. efficiency of belt-driven centrifugals is 72%; electrically driven, 53%; water-driven (H_2O supplied by steam pump) 45%, and water-driven using elec. operated centrifugal pumps, 23%. The steam-turbine-driven machine has a mech. efficiency of 97%. Because of its simplicity of construction it is probably superior to the other types.

W. L. BADGER

Preparation of ores and chemicals by flotation. I. TRAUBE. *Chem. App.* **10**, 117(1923).—A mixt. of oil and H_2O has been successfully used for the quant. sepn. of certain chemicals, such as anthracene from naphthalene, carbazole from alizarin, etc.

J. H. MOORE

Acid- and rust-proof materials for chemical works. REX FURNES. *Chem. Age* (London) **9**, 198-200(1923).—A description is given of the more important acid- and rust-proof materials together with a discussion of the chemical properties which are demanded.

E. H.

Factories and workshops: annual report for 1922. Notes on chemical conditions and processes. ANON. *Chem. Age* **9**, 142-5(1923).—An abstract reviewing reported cases of Pb-, P-, As-, and Hg-poisoning, and other occupational diseases. The increase in the number of cases during the year is due rather to increase in employment than to laxity in precautionary measures.

W. H. BOYNTON

Some moisture relations of colloids. II. Further observations on the evaporation of water from clay and wool. E. A. FISHER. *Proc. Roy. Soc. (London)* **103A**, 664-75(1923); cf. *C. A.* **17**, 2466, 2528.—The study of the evapn. of H_2O from colloid materials has been extended to kaolin and a ball clay. When the rate of evapn. is plotted against moisture content, the curve for ball clay does not show the curvature previously noted in a clay subsoil and attributed to shrinkage, although the ball clay also shrinks. This type of curvature is found only with materials which are mixts. of colloidal and non-colloidal substances, and is due to the simultaneous evapn. of imbibitional H_2O held by the colloid and of interstitial H_2O held as H_2O wedges between the soil grains. The former H_2O evaps. at a practically const. rate, while the latter evaps. at a rapidly diminishing rate. The bearing of these results on the evapn. of H_2O from wool fabrics is discussed.

F. L. BROWNE

Purification of liquids by simultaneous action of centrifugal and electric forces. ALFRED MARX AND JEAN ROZIERES. *Chimie et industrie* **10**, 218-20(1923).—See *C. A.* **17**, 2758.

A. PAPINEAU-COUTURE

Designing and operating a slag-wool plant. HERBERT LANG. *Chem. Met. Eng.* **29**, 365-7(1923).—L. discusses the characteristics of the slag, furnace, slag stream and air-blast that result in a satisfactory slag-wool free from pellets and color. The slag should have as great a range as possible between "appreciable viscosity and fluidity" and should be low in Fe and S. The SiO_2 in the most satisfactory slags is not much over 40%. Such slags are produced in smelting Cu, particularly in pyritic smelting; these produce the softest and longest fibers, and contain only a small amt. of S. Particulars of operation with an oil-fired furnace, using suction fans, are given. The insulating value of slag-wool is almost entirely dependent upon the air enclosed by the mass of fibers. Compression of the mass, by decreasing the % of enclosed air, decreases the insulating properties.

E. G. R. ARDAGH

Hydrogen sulfide as an industrial poison. R. R. SAYERS, C. W. MITCHELL AND W. P. YANT. *Bur. of Mines, Repts. of Investigations* **2491**, 6 pp.(1923).—Two types of H_2S poisoning are noted: acute (asphyxiating) and subacute (inflammatory). Both

types were produced experimentally and studied. Harmful after-effects were more common in cases of severe subacute than severe acute poisoning. Artificial respiration and treatment with O are advised. A table is given showing the relative toxicity to different animals.

JAMES A. BRADLEY

Industrial medicine in Great Britain. Lead poisoning, anthrax, cancer. T. M. LUGGE. *Nation's Health* 5, 371-3(1923).—The industry of ship-breaking or scrapping of war craft has been the source of a no. of cases of Pb poisoning. In cutting the plates by C₂H₂ torch a layer of red lead 1/8 of an inch in thickness on the back of the plates was more or less volatilized so that absorption was by way of the respiratory tract. Some of the workmen developed symptoms like those of "brass founder's ague" which were caused by breathing Zn or ZnO fumes which were evolved from the path of the torch flame. Instructions to printers how best to avoid Pb poisoning are given. These are based on the facts that Pb poisoning is usually caused by inhaling Pb dust and never directly through the skin. Directions for avoiding anthrax disease are given in detail. The relations of cancer to shale oil, lubricating oils and paraffins are discussed.

L. W. RIGGS

Mitteilungen des chemisch-technischen Instituts der Technischen Hochschule, Karlsruhe (Baden). Edited by Paul Askenasy. Halle (Saale), Mühlweg 19: Wilhelm Knapp, Verlagsbuchhandlung.

BLÜCHER, H.: **Auskunftsbuch für die Chemische Industrie.** Vol. I A-L. Vol. II M-Z. Berlin: W. de Gruyter & Co. Vol. I, 840 pp. Vol. II, 832 pp. 11s. each. Two vols. 22s.

LANGÉ, OTTO: **Chemisch-Technische Vorschriften. Ein Handbuch der speziellen chemischen Technologie insbesondere für chemische Fabriken und verwandte technische Betriebe enthaltend Vorschriften aus allen Gebieten der chemischen Technologie mit umfassenden Literaturnachweisen.** Vol. I. Metalle und Minerale. LEIPZIG: OTTO SPAMER. 1011 pp. (32s., bound 36s.) Paper \$8, cloth \$9. Reviewed in *Ind. Eng. Chem.* 15, 982; also in *J. Franklin Inst.* 196, 412(1923).

MACGILLIVRAY, R. J.: **Some Aspects of the Law of England Affecting Chemists.** London: Issued by the Inst. of Chemistry of Great Britain and Ireland. 48 pp.

Ueber Naturprodukte. Festschrift zum 70 Geburtstag Max Honig. Edited by B. M. Margosches and W. Fuchs. Dresden and Leipzig: Verlag von Theodor Steinkopff. 181 pp. 4s. 4d. unbound. Reviewed in *Chem. News* 127, 31; also in *Chemistry and Industry* 42, 737(1923).

Evaporation. C. A. BERGH. Swed. 52,576, Aug. 30, 1922. The soln. is at first evapd. to a suitable concn. in a boiler. The vapors are conducted to a rotary drier, formed as a ball mill provided with a steam jacket or steam spirals, and utilized there for evapg. to dryness the concd. soln. from the boiler.

Evaporating liquids containing easily decomposable organic substances, for instance sulfite waste liquors. AKTIEBOLAGET REYMERHOLMS GAMLA SPRITFOERÅDLINGS. Swed. 52,734, Sept. 20, 1922. The liquid flows with great velocity in thin layers that are passed on all sides by the heating medium. The velocity and the temp. are regulated so as to counteract the formation of crusts on the heating surfaces. The pressure is kept sufficiently high to avoid any boiling inside the heating app.

Separating liquids by distillation. A. J. M. RIALLAND. Brit. 193,030, Jan. 31, 1923. Miscible liquids, e. g., petrol and lubricating oil, are sepd. by atomizing the mixt., which may be preheated, into a gas or into the vapor of a liquid, such as H₂O, with which the constituents of the mixt. are not miscible, and passing the atomized mixt. through a tube divided into regions of progressively lower temp. in which different fractions are sepd. Cold H₂O may be injected into the final region. The different temps. may be obtained by placing jackets round the various parts of the tube and passing steam through the jackets in succession, the steam being allowed to expand in its passage from one jacket to the next.

Destructive distillation of liquid materials. H. O. V. BERGSTROEM. Swed. 51,801, May 31, 1922. The distn. is carried out in 2 steps: At first to sirupy consistency in a stationary vessel which may be heated from without, and finally to complete destruction in a rotary drum.

Separation of mixtures of liquids. H. O. V. BERGSTROEM. Swed. 51,344, Apr. 5, 1922. To sep. one or more very volatile compds. from a mixt. of liquids they are sepd. in an ordinary continuous column app. to a convenient concn. and then the condensate is worked to the desired concn. in another column app.

Separating volatile substances from the condensate of intermittently departing

vapors. H. O. V. BERGSTROM. Swed. 51,455, May 19, 1922. The vapors are accumulated in a vapor container from which they can be removed and used for distg. off the volatile substances from the condensate.

Separating volatile compounds from a mixture of liquids. E. S. SANDBERG. Swed. 53,940, Mar. 7, 1923. The mixt. is heated to a temp. at which vapors are produced. These vapors are brought into contact with chem. reagents that absorb those compds. which should be sepd., while the residual vapors are again forced through the first-mentioned mixt., and so on in a circle process.

Pulverizing resins, paraffin wax, etc. H. EDHOLM. Swed. 50,604, Jan. 18, 1922. The substance is melted and emulsified by means of a convenient agent such as a soln. of glue, starch, etc. The emulsion is cooled below the m. p. of the substance, which is then sepd. from the emulsifying agent.

Boiling by indirect steam. R. A. HULT. Swed. 52,617, Aug. 23, 1922. In the system of boilers groups of steam-spirals are connected in such a way that they can be coupled either in parallel or in succession. The spirals of each individual group are coupled in parallel.

Apparatus for separating the oil from oily waste. F. O. E. BOHLIN. Swed. 52,158, July 12, 1922. The oily materials are treated with steam in a centrifugal machine. The mixt. of oil and condensed water flows directly into a separator by which the oil is sepd. from water and solids in ordinary ways.

Dispersing apparatus for viscous solutions. AKTIEBOLAGET INDUNSTARE. Swed. 52,634, Sept. 6, 1922. The soln. is fed into the narrow lower part of a rapidly rotating funnel and is dispersed by the centrifugal force into a thin layer as it moves up the walls of the funnel. The app. can be used to facilitate the evapn. of viscous solns.

Arrangement on pressing-rollers for the manufacture of briquets. AKTIEBOLAGET LAVAL-BRIKETTRESSEN. Swed. 53,172, Dec. 12, 1922.

Mica, asbestos, and like compositions. PLAUSON'S (Parent Co.), LTD. Brit. 193,520, Nov. 29, 1921. Residues of mica, asbestos, talc, and similar silicates are partly or wholly converted into the colloidal state by high-speed mech. disintegration, preferably in a colloid mill as described in 155,836 (C. A. 15, 1788); the colloidal soln. is subjected to ultrafiltration, dried *in vacuo*, and molded under pressure. Dispersion-accelerators such as colloidal silicic acid, alkali silicates, colloidal ZnO, aluminates, sulfite-cellulose liquor, gum arabic, and tannin may be employed. Fillers or binding agents such as rubber, natural or artificial resins, drying oils, olein, and finely divided clay may be added to the silicate either before or after disintegration.

14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW AND G. C. BAKER

Chemical analysis of water from caravan wells in Arabia. GEORGIADIS. *J. pharm. chim.* 27, 497-502(1923).—Examn. of 7 waters of ill-defined origin, probably from shallow wells, not more than 1.5 m. deep, showed, in g. per l., ext., 0.495-3.300; alky. (as Na_2CO_3) 0.106-0.333; NaCl, 0.163-1.170; SO_4 , 0.037-0.878; CaO, 0.055-0.462; MgO 0.016-0.095; nitrates, 0.015-0.360; phosphates, none, or traces; total hardness, 10.5° to 108°. The waters are evidently solns. of minerals from the surface soil.

S. WALDBOTT

Purifying industrial water. D. H. KILLEFFER. *Ind. Eng. Chem.* 15, 915-7 (1923).—A general discussion is given of the character of water from different sources, softening by pptn. and zeolite methods, and uses of treated water for various industries.

G. C. BAKER

Purification of boiler water. F. H. RHODES. *Sibley J. Eng.* 73-6(April 1923); *Water & Water Eng.* 25, 265(July 20, 1923).

JACK J. HINMAN, JR.

Sterilization of drinking water with chlorine. J. VERSLUYS. *Arch. Suikerind.* 31, 687-96(1923).—Chlorination is used in the purification of river water at Soerabaia, Java. From 0.75 to 1, and at times 1.7 g. of Cl are added per cu. m. of water; the excess Cl is removed with Na sulfite.

F. W. ZERBAN

Chicago menaced by goiter. ANON. Chicago Dept. of Health, *Weekly Bull.* 17, No. 34 (new series) 137-44 (Aug. 25, 1923).—A general review of the subject of goiter as applied to Chicago conditions. Lake Michigan water contains 0.281 to 0.681 part. 1 per billion (McClendon) and it would cost \$57,120 a yr. for NaI sufficient to bring the I content up to $1/16$ gr. per gal. Chocolate tablets containing $1/8$ gr. I as an org. iodide are recommended. Children take 1 tablet a week for 40 weeks. J. J. H., Jr.

State sewage investigations. WM. RUDOLPHS. *Public Health News* (N. J.) 8, 535-8 (July 1923).—A short account is given of biological investigations carried out to det. the organisms responsible for the purification of sewage. J. J. H., JR.

Camp sanitation appliances. ANON. *Public Health News* (N. J.) 8, No. 7, 462 (June 1923).—Boiling in preference to $\text{Ca}(\text{OCl})_2$ treatment is recommended as more likely properly to be carried out to safeguard the water supply on a small scale. JACK J. HINMAN, JR.

School sanitation. H. E. MILLER. *Health Bull.* (N. C.) 38, No. 9, 28-31 (Sept. 1923).—Proper attention should be paid to the water supply, common drinking cup, drinking fountains and excreta disposal. JACK J. HINMAN, JR.

Underground ventilation at Butte. DANIEL HARRINGTON. *Bur. of Mines, Bull.* 204, 127 pp. (1923).—The dust situation has been largely eliminated by the adoption of wet drills and by the introduction of water lines for sprinkling the working faces. Increased flow of air removes dust as formed. The study made covered general mining conditions, mining methods, present ventilation, factors influencing temp. of mine air, humidity, compn. of air, etc. Recommendations are made. H. C. PARISH

The H-ion concentration of natural waters and some etching reagents in relation to action on metals (ATRINS) 9.

FOLWELL, A. PRESCOTT: *The Designing, Constructing and Maintaining of Sewerage Systems and Sewage Treatment Plants.* 9th Ed. Revised. New York: John Wiley & Sons; London: Chapman & Hall. 477 pp. \$4. Reviewed in *Proc. Am. Soc. Civil Eng.* 49, 446 (1923).

HARRIS, F. W.: *Report on the Activated Sludge Process of Sewage Purification: Its Efficiency and Applicability to the Glasgow Works.* Glasgow: Robert Anderson. 24 pp.

Chlorinating water, etc. WALLACE & TIERNAN CO., INC. *Brit.* 193,032, Feb. 2, 1923. App. for chlorinating H_2O , etc., comprises a bell jar standing in a tray of H_2O to which Cl is admitted from a container through a tube and a valve controlled by a float. The Cl is withdrawn from the bell jar through a small calibrated aperture at the top of a tube and passes through a concentric tube to an aspirator through which the H_2O to be treated passes on its way from a supply pipe to a discharge pipe. A suitable construction is specified.

Treating colloidal and putrescible organic matter. F. R. O'SHAUGHNESSY. *Brit.* 193,477, Nov. 22, 1921. An activated sludge for use in the treatment of org. matter, such as sewage sludge, carcasses and putrefying food, is prepd. by maintaining some crude sludge at a temp. of not less than 15.5° in a tank of much greater vol. through the upper part of which slightly alk. H_2O , which may contain colloidal org. matter, is continuously passed. The activated sludge may be mixed with sludge to be treated by pumping the activated sludge into the pipe through which the other sludge passes to a primary treatment tank. The treatment tank is kept at a temp. of 10° to 15° and a portion of its contents is removed from time to time to a secondary treatment tank, in which the liquid seps. from an inoffensive non-colloidal sludge, which when dried is suitable for use as *fertilizer*. Large masses of waste or putrid matter, such as carcasses, are digested in tanks contg. a substantially greater vol. of the activated sludge.

15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

The use of calcium carbonate in nitrogen fixation experiments. P. L. GAINNEY. *J. Agr. Research* 24, 185-9 (1923); cf. *C. A.* 17, 2931.—The no. of soils capable of initiating the growth of *Azotobacter* under the conditions investigated was greater by 20% when CaCO_3 was added to the medium than when it was omitted. The quantity of N fixed in a medium contg. CaCO_3 was also observed to be always equal to and in most cases greater than when CaCO_3 is not present. The presence of CaCO_3 exerts a greater beneficial effect upon those organisms other than *Azotobacter* that bring about the fixation of N than upon *Azotobacter* itself. W. H. ROSS

A study on the effect of changing the absolute reaction of soils upon their *Azotobacter* content. P. L. GAINNEY. *J. Agr. Research* 24, 289-96 (1923); cf. preceding abstr.—If 2 soils, one more acid than pH 6.0 and contg. no *Azotobacter* and the other less acid

than p_H 6.0 and contg. this organism, are mixed in varying proportions, incubated for some time and cultured for *Azotobacter*, all mixts. giving an acidity less than p_H 6.0 will show the presence of *Azotobacter* while all cultures very much more acid than p_H 6.0 will fail to do so. A soil more acid than p_H 6.0 will support *Azotobacter* if sufficient $CaCO_3$ is added to reduce the H-ion concn. to less than p_H 6.0, and conversely if sufficient acid is added to a soil less acid than p_H 6.0 to increase the acidity to a point very much greater than p_H 6.0, any *Azotobacter* present will disappear from the soil provided this acidity exists for sufficient time to complete their destruction.

W. H. ROSS

Influence of the hydrogen-ion concentration on the growth and fixation of nitrogen by cultures of *Azotobacter*. P. L. GAINES AND H. W. BATCHELOR. *J. Agr. Research* 24, 759-67(1923); cf. preceding abstrs.—The data point very definitely to a limiting H-ion concn. of p_H 5.9 to 6.0 for the various cultures of *Azotobacter* employed when grown under the conditions of these expts. Vigorous growth and N fixation took place at p_H 6.1 to 6.5, the optimum p_H for N fixation apparently being somewhat higher than the optimum for growth. Very slight if any changes in the reaction of the media are produced by the growth of the various strains of *Azotobacter* studied, indicating the production of inappreciable quantities of acid or basic metabolic by-products. The results found for pure cultures agree very closely with those previously found in soil expts. and tend to substantiate former conclusions that this group of organisms will not exist and function in soils whose H-ion concn. is greater than p_H 5.9 to 6.0. Cf. C. A. 16, 3101.

W. H. ROSS

Oxidation of sulfur by microorganisms in black alkali soils. S. A. WARSMAN, C. H. WARR, JACOB JOFFE AND R. L. STARKEY. *J. Agr. Research* 24, 297-305(1923). The use of S in the presence of the proper S-oxidizing bacteria will result in the transformation of black alk. soil to white alk. soil. The final reaction of the soil depends on the quantity of S used and the length of time which the S is allowed to be in contact with the soil. The oxidation of S in black alk. soil is probably carried on by the agency of more than one S-oxidizing bacterium. In the presence of 2 bacteria, one of which can act upon S under distinctly alk. conditions while the other rapidly oxidizes S under acid conditions, the speed of the reaction is greatly hastened.

W. H. ROSS

The Apulian hardpan and its origin. II. A. DE DOMINICIS. *Ann. scuola agr. Portici* [2] 16, 18 pp.(1920); cf. C. A. 16, 606.—The studies on the hardpan of the Bari district are here extended to the remainder of Apulia, where the hardpan rests on a more or less finely divided, friable, calcareous soil into which roots easily penetrate instead of adhering firmly to strata of calcareous tufa forming the compact, rocky subsoil in the Bari area. The position of the hardpan, the conditions of its existence, its compn., its properties and all the factors bearing on its origin and the consequences of its possible removal were studied on the spot. The results of these new expts. generalize the significance of the previous ones and show that the hardpan is not a special phenomenon of massive, rocky subsoils. They prove that the formation of the Apulian hardpan in particular and of superficial hardpans of a calcareous nature in general always depend on the same conditions: (a) localization at the plane where soil and subsoil come in contact, (b) a subsoil, with an active capillary system permeating a mass rich in $CaCO_3$, in an arid climate, (c) a soil and a circulating soln. provided with sufficient colloidal material in the state of reversible hydrogels and hydrosols, the capillary liquid being laden with $CaCO_3$, (d) the co-existence of all these conditions. This entails: (1) the following properties in common, (a) a permeability limited to the first moments of the action of the H_2O and detected only by special methods, (b) a capillarity not extending beyond the outer thin layer of the hardpan; (2) similar chem. constitution consisting in (a) $CaCO_3$ derived from the subsoil, (b) ingredients of a clayey and sandy nature which are derived from the soil. The mechanism of the formation of hardpan is thus always the same and is to be attributed to the reactions of a colloidal nature which occur when the hydrosols of the circulating soln. meet the bivalent electrolyte, $CaCO_3$, of the capillary soln. and to the energetic absorbent power which the resultant coagulated mass exhibits towards the $CaCO_3$. These principles are supported by the new facts revealed by these researches.

ALBERT R. MERZ

Relation between the indican content of Java indigo (*Indigofera arrecta*) and the kinds of nitrogenous fertilizers. N. V. JOSHI. *Proc. Asiatic Soc. Bengal, Proc. 8th Indian Sci. Cong.* 17, lxxxvii-iii(1921).—Pot culture expts. on fertilizing indigo have been carried out to ascertain the effect of the nitrogenous fertilizers and inoculation of different nodule organisms on the indican content of the leaf. For this purpose indigo has been grown under controlled conditions in sterile sand as also in Pusa soil. Conclusions: Addn. of nitrates gives the largest increase in the % of indican in the indigo leaf. The increase in indican content is much less in all other treatments, viz., the addn.

of NH_3 , sterile plant ext. and the inoculations with different nodule organisms. All these treatments, however, have a tendency to increase the leaf growth, sometimes to such an extent as to compensate for the lower % of indican. Addn. of cow manure and cow manure plus straw gives a poor growth of indigo plants as well as low % of indican in the leaf in the first cutting, showing that the N in these cases is not immediately available for assimilation by the plants. In the *khunti* crop addn. of cow manure plus straw shows remarkable increase in leaf growth accompanied by low % of indican, which effect is similar to that of the addn. of NH_3 or inoculation with nodule organisms.

H. G.

Measuring soil temperature by standard thermometer suspended in iron pipe. A. B. CONNELL. *Ecology* 4, 313-6(1923).—The object was to det. the relative value of the thermometer enclosed in a special form of iron pipe for measuring soil temp. at a depth of 2 ft., as compared with the standard soil thermometer. The agreement in results was so close that for all ordinary purposes the instrument described may be used.

L. W. RIGGS

Influence of concomitant conditions on the toxicity of black alkali. A. E. VINSON AND C. N. CATLIN. *Arizona Sta. Rept.* 1921, 558-9; *Expt. Sta. Record* 48, 422.—Progress results of these studies are briefly noted. With concns. of Na_2CO_3 as low as from 0.05 to 0.075% sorghums made very weak growth. With winter cultures wheat proved much more resistant to black alkali than barley. Sand mixed with alkali soil greatly intensified the toxicity of the black alkali, while clay had a neutralizing effect.

H. G.

A preliminary note on the theory of phosphatic depletion in the soils of Bihar. ALBERT HOWARD AND G. L. C. HOWARD. *Agr. J. India* 18, 148-54(1923).—Expts. conducted to det. the nature of the apparent deficiency of available phosphate in certain calcareous soils of Bihar show the phys. condition of the soil to be the main source of the apparent infertility. The improvement brought about by superphosphates on those soils was due to the acidity produced. Similar and even better results were obtained by the use of dil. H_2SO_4 or S. S produced a slower but more permanent effect, especially if combined with a system of green manuring.

RUSSELL M. JONES

Agrologic and agrolgic survey of the Setif region. I. POUGET, ALAMERIC, AND LÉONARDON. *Univ. Alger Lab. Chim. Appl. Facult. Sci.* 1922, 73 pp.; *Expt. Sta. Record* 48, 420.—Mech., phys., and chem. analyses of the prevailing soil types are presented and discussed. The best agricultural soils are the black marl soils of the northern and central parts of the area and the alluvial soils. These soils are deep and contain a large percentage of fine materials, which permit the retention of a sufficient reserve of moisture. The red calcareous silts are of lesser depth and have a lower moisture-retaining capacity, and in the more arid regions the crop yields are sparse. The soils of the area are said to be generally well supplied with plant nutrients. The N content is rarely lower than 1%, and soils deficient in P_2O_5 are very rare. The soils are also well supplied with K and Mg. These great reserves of N and P_2O_5 are frequently in more or less unavailable form, so that returns have been realized from nitrogenous and phosphatic fertilization of a more available nature. The apparent limiting factor in soil fertility in the area is moisture. This can be materially improved by developing the org.-matter content of the soils.

H. G.

Adsorption on soil grains. G. A. J. COLE. *Nature* 112, 205-6(1923).—A discussion of the work of Anderson, Frye, Gile, Middleton and Robinson (cf. C. A. 17, 322). The criticism is made that the artificially crushed material would not be quite comparable with the natural soil material, e. g., quartz and garnet probably do not present so large a surface in comparison with other minerals and limonite is probably present in a much finer form than is suggested.

H. M. McLAUGHLIN

The pseudo-antagonism of sodium and calcium in dilute solutions. H. S. REED AND A. R. S. HAAS. *J. Agr. Research* 24, 753-7(1923).—Citrus seedlings grown in absence of Ca soon show injury to the root systems as evidenced by the gelatinization of the superficial layers and the ultimate death of the root. The tops however may not show the effect for some time after the injury to the roots has become severe. If the injury has not progressed too far the addn. of Ca to cultures in which the roots are gelatinized induces the production of lateral rootlets. The varieties of citrus studied possess a marked capacity for the absorption of Ca ions. Hence in very dil. solns. the amts. present may be too far below the equil. point within the plant to avoid a condition of starvation. In such cases the condition is due not to the lack of ions which antagonize the Na but rather to Ca starvation. The expts. with citrus seedlings have thus not demonstrated the existence of antagonism between Na and Ca when the plants are grown in very dil. solns.

W. H. ROSS

Nutrition of plants considered as an electrical phenomenon. J. F. BREAZEALE. *J. Agr. Research* 24, 41-54(1923).—A demand for plant food may be developed in the tissues of plants and this demand may be measured by analytical methods. The demand of the plant seems to be for particular foods and the effect of any application of plant food as a fertilizer seems to be largely a direct action upon the plant itself and not on indirect action upon some constituent of the soil. Plants probably feed upon ions and these ions probably penetrate the root membrane and move through the colloids to the tissues as an elec. charge; therefore the feeding of plants may be looked upon as an elec. phenomenon. Ions are mobile and may move through the soil soln. freely as such; and this being the case the plant may not be dependent upon the soil grains that touch its roots for nutrient material but may feed at a distance from the source of supply.

W. H. ROSS

New phosphoric acid fertilizers. P. KRISCH. *Kali* 17, 151-4(1923).—The prepn., compn., and fertilizing value of "Sinter phosphate," "Kolloidal phosphate," ground phosphate rock and S mixts., "Phosphate-humus," and "Ephos basic phosphate" are briefly discussed.

K. D. JACOB

"Superam," a new compound fertilizer. CAMILLE MATIGNON. *Chimie et industrie* 10, 216-7(1923).—"Superam" is prepd. by passing dil. (3-5%) NH_3 gas over superphosphate so as to obtain: $\text{H}_3\text{P}_2\text{O}_4 + 2\text{NH}_3 = (\text{NH}_4)_2\text{HPO}_4 + \text{CaH}_2(\text{PO}_4)_2 + 2\text{NH}_4 = \text{CaHPO}_4 + (\text{NH}_4)_2\text{HPO}_4$, avoiding formation of $\text{Ca}_3(\text{PO}_4)_2$. Fixation of NH_3 is accompanied by a slight rise in temp., which must be carefully regulated and which gives a drier and more easily handled product than the original superphosphate. A typical analysis is: ammonia N 4.10, total P_2O_5 15.77, available P_2O_5 15.30, water-sol. P_2O_5 11.95%. The superphosphate can be over-acidified and the excess acidity neutralized with NH_3 , giving a higher NH_3 content than with ordinary superphosphate.

A. PAPINEAU-COUTURE

Mills for Thomas slag. H. HERMANS. *Met. italiana* 15, 112-25(1923).—Descriptive, with illustrations and sketches.

ROBERT S. POSMONTIER

The protective significance of Uspulun, especially as a seed treatment. G. KOCK. *Zentr. Agr. Chem.* 50, No. 4, 134-40(1921); *Expt. Sta. Record* 48, 241-2.—Uspulun, contg. Na_2SO_4 , NaOH , aniline, and mercury chlorophenol (the last named being the principal effective component), is discussed as to its compn. and its fungicidal effects, and also its influence on germination. Germination was depressed by high concn. Uspulun also decreased smut infection of wheat. Experimentation with other crops is briefly discussed.

H. G.

Testing of dip fluids. C. WILLIAMS. *J. Dept. Agr. Union S. Africa* 7, 86-7(1923).—The importance of accurate cstn. of the strength of dipping fluids is emphasized. The standard I soln. used in com. "testers" must be preserved in dark bottles with tight-fitting glass stoppers and stored in cool dark places. Org. matter in dipping fluids is best pptd. before testing by the addn. of a small amt. of a thick paste of HCl and NaCl or H_2SO_4 and NaHSO_4 . It is absolutely essential that free acid in the clarified dip be neutralized with a slight excess of NaHCO_3 before addn. of the I soln. If the clarified dip is highly colored, starch paste or paper should be added as an indicator. The ordinary "testers" do not register the presence of arsenate and chem. analysis should be employed to det. its presence.

K. D. JACOB

Action of soap on lead arsenates. R. M. PINCKNEY. *J. Agr. Research* 24, 87-95(1923).—Solns. of Na stearate and oleate soaps dissolve As from lead arsenate but the former soap dissolves from 2 to 7 times as much As as the latter. The As of diplumbic arsenate is much more acted upon than the triplumbic orthoarsenate. Increasing the concn. of the stearic soap soln. increases the amt. of As made sol. The amt. of As which this soap soln. dissolves from diplumbic arsenate is much too great to confirm the supposition that its action stops with the conversion of diplumbic into basic lead arsenate, and it is concluded that the action of soap upon lead arsenate is of the double-decompn. sort.

W. H. ROSS

The culture of *Pyrethrum cinerariaefolium* in France and the preparation of pyrethrum soap for agricultural purposes. A. J. VAN LAREN. *Pharm. Weekblad* 60, 877-92(1923).—A description of the methods of culture as recommended by the French officials. The soap is prepd. by extg. the blossoms with EtOH or other suitable solvent, distg. off the solvent and dissolving the resinous residue in a soln. of green soap. 100 kg. of the blossoms yields 650 kg. of pyrethrum soap, which dild. 1:10 is used as an insecticide and fungicide by the wine growers.

A. W. DOX

Pharmacodynamic action of the insecticide from the flowers of *Pyrethrum* (CHEVALIER, MEXICANA) 11H. Treating phosphorous iron ore (Swed. pat. 52,399 and 52,400) 9.

Soil-improving composition. P. HESSELIUS. Swed. 52,637, Sept. 6, 1922. Dried pine-needles and branches and other wood wastes are mixed with earth or black mold and heated to redness until the ligneous substances are completely carbonized.

Phosphorous fertilizer. AKTIEBOLAGET ALKALIVERKEN. Swed. 54,116, Mar. 28, 1923. Raw phosphate is decompd. by a mixt. of HCl and H₂SO₄ obtained by the action of Cl₂ (from alkali chloride electrolysis) upon aq. SO₂.

16—THE FERMENTATION INDUSTRIES

C. N. FREY

Denatured alcohol in Canada. R. E. GILMORE. *Chemistry & Industry* 42, 802-8 (1923).—See *C. A.* 17, 2342, 2628. E. J. C.

Analytical characteristics of French liqueur wines. LUCIEN SEMICHON. *Ann. fals.* 16, 333-40(1923).—"Liqueur wines" are defined as contg. at least 14-5% alc. and a considerable amt. of unfermented sugars. They can be prepd.: (1) by overmaturing or natural concn. of the grapes or of the musts ("vins liquoreux"); (2) by addn. of not more than 10% of alc. to musts having a sugar content equiv. to a possible production of at least 14% of alc. by vol. (semi-sweet wines, "vins demidoux"); (3) by addn. of 15% of alc. to the must to stop or prevent fermentation (sweet wines or mistelles, "vins doux," "mistelles"). S. goes into a simple but somewhat lengthy mathematical and graphical discussion (which cannot be satisfactorily abstracted) of the interpretation of analytical results (alc., unfermented sugars, sugar-free ext.), showing how to distinguish with reasonable certainty between the 3 above classes of liqueur wines. A. P. C.

Investigation into the ripening of grapes. E. MANCEAU. *Ann. fals.* 16, 341-4 (1923).—Ripening of grapes is accompanied by a decrease in acidity and increase in sugar, which reach a min. and a max., resp., which are maintained for a certain length of time at complete maturity. Analyses at 3-4-day intervals for some time before maturity can indicate the approx. date of complete maturity, care being taken to obtain a representative sample and to express the same amt. of juice as would be pressed in the regular wine-making operations. For a given wine detns. of acidity and of d. of the juice are sufficient. A. PAPINEAU-COUTURE

Sulfuring of wine. C. VON DER HEIDE. *Wein u. Rebe* 3, 571-95(1922).—The proposed changes in the regulations concerning the sulfuring of wines in Germany are considered. Several methods are described and the action of sulfuring on wine is discussed. J. S. C. I.

Dried (brewers') grains. H. E. DRYDEN. *J. Inst. Brewing* 39, 51-7(1923).—The squeezings obtained from wet brewers' grain before these pass into the drier amount to about 100 gal. per ton of dried grain, and contain 5-6% of fine solid matter having a food value much higher than that of the dried grains. The latter contain about 6.1% of oil, 19.5% of protein and 43.8% of digestible carbohydrates; the corresponding analyses for the solid squeezings give 8.5%, 27.8% and 38.3%, 12% of H₂O being allowed in each case. Methods for the sepn. of the solid matter are given. Dried grains from a mash contg. flaked maize show a higher percentage of oil than those from an all malt mash. Barley yields about 1/4 of its wt. of dried grain. J. S. C. I.

The maximum sulfate content of wines produced by means of the plastering of the grape. ARTURO BORNTRAEGER. *Ann. scuola agr. Portici* [2] 16, 1-32(1920).—The highest degree of plastering (measured by the K₂SO₄ in the wine) obtainable by B. with grapes from the Vesuvian region was 7.36 per 1000. ALBERT R. MERZ

Can wines, plastered to the extreme, contain potassium bisulfate? ARTURO BORNTRAEGER. *Ann. scuola agr. Portici* [2] 16, 1-35(1920).—The results of 2 series of expts. on the preservation of strongly plastered wines (5.6 and 5.8 per 1000) were concordant in that even after several years the liquids still gave ashes with real, although small, alk. This corresponded to 0.5165 and 0.5346 per 1000 of K₂CO₃, notwithstanding the first wine had been cooled to -2° and the other to 2°. With Neapolitan grapes, very strongly plastered wines contg. bisulfate could not be gotten either directly or as a result of keeping during the winter or even rather strong cooling (-2°). On the contrary satn. of all the bases with mineral acids could not even be attained. A. R. M.

Investigation of the inorganic acids in wine. E. GARINO-CANINA. *Staz. sper. agrar. ital.* 55, 89-104(1922).—On comparison of the compn. of 2 wines their acid energy appeared decidedly different; C_H was 1.10 and 0.106, resp. The very low value for the latter wine is explained by the strongly inhibiting action on electrolytic dissociation of the N⁺I₂ which this wine contains in excessive and abnormal quantity and also by the

little free titratable acidity as compared to that combined as salts. The tartaric acid is completely or almost completely combined as salts and the other acids also are combined as salts to an extent unknown in Italian wines. The electrochem. method is the only one that can give certain results in the investigation of mineral acids and their mixts. in wine, a clear distinction between plastered bitter wines and those treated with inorg. acids not being possible by means of chem. results alone. This method can be applied to *vinegars, beers and ciders* as well as to wines.

ALBERT R. MERZ

Influence of sulfur dioxide in the determination of the volatile acidity of wines. E. GARINO-CANINA. *Staz. sper. agrar. ital.* 55, 80-8(1922).—The presence of SO_2 in wines can cause considerable error in the detn. of volatile acidity. This influence is most in those wines which, by being near the max. limit of volatile acidity tolerated, can by small variations be qualified as unsuitable for consumption, the more so since sulfites are added to such wines in considerable proportions for curative or preventive purposes. The cor. acetic acidity is, however, important, if only theoretically, when it is a question of establishing the balance of the org. and the fixed and volatile acids, in which case it is best to deduce the equiv. SO_2 from the sulfates detd. gravimetrically in the distillate. The Cazenueve volatilitimetric app. gives good results and should find a place beside the Malligand ebulliscope as a valuable technical instrument for the control of the fermentation and the preservation of wines.

ALBERT R. MERZ

Amount of arsenic in grapes, must and wine resulting from treatment of the vines with arsenical sprays. C. VON DER HEIDT. *Wein u. Rebe* 3, 515-28, 595-6(1922).—Gathered grapes, pressed must, pressed marc, new wine yeast, and marc-wine, and marc-wine yeast were tested for the presence of As after the vines had been subjected to treatment with Pb arsenate ("Zabulon"), Ca arsenate (Sturm's material), and Cu acetoarsenite (Schweinfurth's green or, if very finely divided, urania green). As was detected in all the samples examd., even when it had not been administered to the vines. In general grapes treated with urania green contain more As than those treated with "Zabulon," and rotten-ripe grapes more than normal ones. The proportions of As present in the wines were 0.02-0.18 mg. per l., and should thus be harmless. The wine yeasts, however, contained as much as 0.185 g. of As per kg. of dry matter, such an amt. being harmful to animals. With marc-wine yeast 0.1456 g. of As per kg. was found.

J. S. C. I.

Use of hydrogen peroxide in the estimation of nitrogen. ROBERT HEUSS. *Woch. Brauerer* 40, 73-4(1923).—The use of H_2O_2 , as suggested by Kleemann (*C. A.* 16, 1196) in Kjeldahl's method for estg. N, is of advantage in the case of barley, the time required for the complete attack of 1.75 g. of the finely ground grain being reduced from 75-90 minutes to 45 minutes. The quantities of the different reagents suggested by Kleemann may be reduced to: 7-8 g. of K_2SO_4 , 20 cc. of H_2SO_4 , and 15 cc. of 30% (by wt.) H_2O_2 soln. A blank estn. must be made with the materials alone and the results corrected accordingly.

J. C. S.

Flaked maize as brewing material. A. E. BERRY. *J. Inst. Brew.* 29, 219-27 (1923).—The compn. of maize no matter from what source does not vary greatly. Finess of flakes is more important in detg. yield of ext., extremely fine flakes of a given wt. yielding 102 lb. ext., thin flakes 99.4, coarse flakes 98.2 and extra large flakes 93.

C. N. FREY

New possibilities of increasing brewer's extract. M. H. VAN LAER. *J. Inst. Brew.* 29, 202-18(1923).—Increasing the H-ion of the mash to pH 5 to 5.4, allowing 2 hrs. at 45° for peptonization, increased the yield of ext. Two malts of over 250 diastatic power, Windisch scale, gave 82.5 and 87.6 lb. ext. per quarter, calcd. on malt, with coarse grinding, 91.1 and 92.2 with fine, and 97 and 98.1 when acidified. The increase in yield is comparable to that obtained by fine grinding. If the temp. is the same the principal change with increased acidity is increase in maltose at the expense of dextrin. The amt. of maltose can be controlled by raising the temp. The additional ext. obtained by saccharifying in more acid solns. contains 50 to 57% sugar and 30 to 40% nitrogenous matter.

C. N. FREY

Cholam (*Andropogon sorghum*) as a substitute for barley in malting operations. R. V. NORRIS AND B. VISWANATH. *Agr. J. India* 18, 362-73(1923).—A comparison is made between cholam and barley malts and also a study of the properties of the former with regard to its suitability in brewing and other operations. The av. chem. compns. of barley and cholam are 12.25, 14.05% moisture; 10.58, 10.58% crude protein; 69.77, 63.66% carbohydrates; 1.58, 7.09% fiber; 4.14, 2.05% fat and 1.68, 2.51% ash, resp. The higher fat content of the cholam tends to reduce the amt. of ext. obtainable from the malt. Cholam malt has high powers of saccharification but comparatively low diastatic activity. This deficiency of diastatic power is relative only and eventually

the sugar production from cholam malt equals or surpasses that from barley malt. Cholam should replace barley for many purposes in India. R. M. JONES

Action of ultra-violet rays on alcoholic fermentation by *Botrytis cinerea*. ROMOLO DE FAZI. *Atti accad. Lincei* [v] 32, 235-6(1923).—Fermentation of must from grapes infected with *Botrytis cinerea* is accelerated by exposure of the must to the light from a quartz mercury vapor lamp. J. C. S.

Enological products—selected yeast. ASTRUC AND CHEVALIER. *Ann. fals.* 16, 351-5(1923).—Comparative analyses of a com. sample of so-called concd. selected yeast and of a wine obtained by fermenting the must to obtain a max. yeast yield showed the latter much superior to the former. A. PAPINEAU-COUTURE

Influence of the alcohol content on the stability of beer. A. AMBERGER. *Woch. Braueri* 40, 92-4(1923).—When malt first became available again in quantity for brewing in Finland after the war it was noticed that the beers of low alc. content, to which brewing was limited by law, were much less stable than the war substitutes, the dark porter type of beer possessing greater stability than the clear Pilsener variety, in spite of the larger quantity of hops used in the production of the latter. This difference in stability was traced to the fact that the acid content of the dark beer was 60% greater than that of the clear product (0.08%, calcd. as lactic acid in the dark variety, as compared with 0.05% in the Pilsener). The turbidity produced on standing for a few days was found to be due to bacteria introduced in the water used for washing out the filters. The ordinary town (Helsingfors) supply was used for this purpose. In a series of expts. it was shown that the stability could be greatly improved by increasing either the alc. or the acid content or both. Normally greater alc. content is accompanied by a proportionate increase in the amt. of acid in the beer. A satisfactory stability can only be obtained with beers of twice the alc. content at present permitted by Finnish law (i. e., 4% instead of 2% of alc. by vol.) and the correspondingly greater acid content. The addn. of acid alone to the weak beers at present brewed produces an unpleasant acid taste, and is therefore out of the question. J. S. C. I.

Titrimetric method for determining specific gravity [of wort] by means of floats. DOEMENS. *Z. ges. Brauw.* 46, 23-9(1923).—A method is described which is more rapid and accurate than the pycnometric method and is free from the surface tension effect introduced by the use of a saccharometer. Into 200 cc. of the wort in a glass cylinder contg. also a hollow glass bead, similar to those employed in regulating the working of a patent spirit still, but fusiform, so as to allow it to rise more quickly, water is run from a buret until the bead just sinks; care must be taken to maintain a definite temp. in the liquid. From the known sp. gr. of the bead, which should be somewhat greater than that of the wort, and the amt. of water added, the sp. gr. of the wort may be calcd. J. S. C. I.

Determination of the evaporation factor, an important point in the judgment of brewer's pitch. B. LAMPE. *Woch. Brau.* 40, 91-2(1923).—A method is described for detg. the "evapn. factor," i. e., the loss of wt. on heating a specimen of pitch at a fixed temp. for a definite time, and the importance of this test in the selection of pitch is demonstrated. In the expts. quoted, whereas one specimen of pitch on heating at 200° for 5 hrs. lost 10.15% by wt., another sample lost only 4.35%. In the first case the m. p. was raised by 5.5° and the viscosity at 200° from 1.51 to 1.65; in the second the rise in m. p. was only 3°, and the viscosity at 200° changed from 1.54 to 1.75. J. S. C. I.

Investigations on the starch-liquefying function of malt diastase. W. WINDISCH, W. DIETRICH AND ARTUR BEYER. *Woch. Brau.* 40, 49-50, 55-6, 61-3, 67-70(1923).—The exptl. results indicate that the liquefaction of starch by diastase probably depends on increase in the degree of dispersion of the starch or amylopectin. The liquefying action proceeds best when p_H has the value 5.03, the reaction being thus similar to the optimum reaction for saccharification of starch by diastase. The method suggested for detg. the liquefying power of malt diastase consists in treating amylopectin made from wheat starch with an aq. ext. of the malt in presence of a buffer mixt. of Na acetate and acetic acid, the filtered liquid being afterwards hydrolyzed by means of HCl and the dextrose thus formed estd. iodometrically. The amt. of starch liquefied by the diastase present in 1 g. of malt is taken as a measure of the liquefying power. Kjeldahl's law of proportionality is found to hold for the liquefying, as well as for the saccharifying power, but the liquefying powers bear no const. relation to the saccharifying powers with different malts. J. C. S.

Influence of highly dilute organic acids on the spore-formation of yeasts. H. LÖFFLER. *Allgem. Z. Bierbrau. Malzfabr.* 50, 127-31(1922).—Low concns. of org.

acids, such as *N*/126 oxalic acid or *N*/15 acetic or tartaric acid, increase the readiness with which culture and wild yeasts sporulate. J. S. C. I.

Precipitation of proteins of barley by electrolytes and its relation to degree of dispersion (WINDISCH, *et al.*) 11A. Influence of Kanbara earth on certain hydrolytic enzymes (KITA, SUZUKI) 11A. Halphen number disk. A practical apparatus for the calculation and rapid application of the Halphen rule [for determining the alcoholic content and Halphen number of wines] (ANON) 7.

Notice of the Oenological Instruments of Precision. Popularising of Oenological Chemistry, Alcohols, Brandies, Vinegars, Ciders, Brewing. Paris: J. Dujardin. 112 pp.

Alcohols from sulfite waste liquor. R. S. SANDBERG, H. A. E. NILSSON and J. V. BLOMQUIST. Swed. 53,317, Jan. 3, 1923. The liquor, after neutralization, is evapd. to a concn. suitable for fermentation, by which evapn. about half of the MeOH of the liquor is obtained in the condensate and is recovered from this. The residue from the first-mentioned evapn. is neutralized, fermented and evapd. EtOH and some MeOH are obtained in the condensate and are sep'd. in a column app.

Manufacture of yeast. E. G. KRONBERG. Swed. 54,489, May 9, 1923. After having finished the proper fermentation of the mash, the yeast cells are allowed to stay in the mash for some time, vegetating on the remaining nutrient materials.

17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

Chemistry in the manufacture of surgical catgut and violin strings. PIO LAMI. *Boll. chim. farm.* 61, 33–42(1922).—A detailed description of the Italian process of manuf. from the fresh sheep intestine to the finished product. The steps involved are: soaking 3–4 days in running water, mech. removal of adipose tissue, soaking 1–2 days in 1% K_2CO_3 soln., then 3 days in K_2CO_3 plus 2–3% NaCl, scraping to remove the mucous layers, soaking 6 days more and gradually increasing the concn. of alkali to 3%, sorting, bleaching with H_2O_2 or Na_2O_2 , twisting, drying, polishing and oiling. A. W. DOX

Chemical analysis of drugs. FRANÇOIS MARTIN. *J. pharm. Belg.* 5, 533–6, 549–51, 565–8(1923).—A scheme for the proximate analysis of vegetable drugs is outlined. The article is too condensed to be abstracted. A. G. DuMEZ

Estimation of aldehydes and ketones in essential oils. C. T. BENNETT AND F. C. L. BATEMAN. *Perfumery Essent. Oil Record* 14, 268–70(1923).—Referring to the recent work by Bennett and Garratt (*cf.* *C. A.* 17, 2629), further comparative expts. are recorded showing the influence of the size of sample, proportion and compn. of the $NaHSO_3$ soln. and the size of flask on the final results. It appears that a 5-cc. sample gives more accurate values than 10 cc. and it is recommended that not less than 50 cc. of a bisulfate soln. contg. little free SO_2 be taken for every 5 cc. of the oil. W. O. E.

Bellary leaf and other Indian oils. ANON. *Perfumery Essent. Oil Record* 14, 271–2(1923).—Phys. consts. are reported for: Bellary oil (from the fresh leaves of *Litsea zeylanica* in a yield of 0.602%), d. 0.890, $[\alpha]_D^{20}$ 1.4980, ester no. 22.6, ester of acetylated oil 81.6. Devadari wood oil from bastard sandalwood (*Frythoxylon monogynum*) in a 0.217–0.27% yield, d. 0.896, $[\alpha]_D^{20}$ 1.5140, ester no. 11.9, after acetylation 106.8. Chigatamari wood oil in a 2.2% yield, d. 0.907, $[\alpha]_D^{20}$ –82° 30', n_D^{20} 1.4965, ester no. 5.5, after acetylation 24.6. Chembaliku wood oil (2 samples) in a 1.65% yield, d. 0.918 and 0.927, $[\alpha]_D^{20}$ –59° and –51°, n_D^{20} 1.4955 and 1.4980, ester no. 5.4 and 12.1, after acetylation 45.1 and 60.9. W. O. E.

Adulterated Burma and Java citronella oils. S. MARSHALL AND M. S. SALAMON. *Perfumery Essent. Oil Record* 14, 254–5(1923).—An account of certain samples adulterated with some fat (probably native but as yet undetd.), which is pptd. on treating the oil with 80% alc. While adulteration to the amt. of 5% or more is not difficult of detection, this would be difficult in the case of bulking samples for such examn., in which event the amt. of adulterant present might be reduced to less than 1%, whereas any one of the constituent samples may have been considerably sophisticated. Several other forms of adulteration (low acetyl value) are noted, but whether due to some adulterant other than fat or faulty distn. is uncertain. W. O. E.

Artificial thymol. W. H. SIMMONS AND F. C. DYCHE-TEAGUE. *Perfumery Essent. Oil Record* 14, 256-7(1923).—An account of the prepn. of this product from piperitone and its comparison with Ajowan thymol. Reference is also made to its manuf. from *p*-cymene via M. Phillips (*C. A.* 17, 2276), and to an English patent (197,848) involving its prepn. from *m*-cresol and isopropyl alc. W. O. E.

Modern technical methods for the manufacture of synthetic perfume. ARTHUR LEWINSON. *Perfumery Essent. Oil Record* 14, 259-60, 291-2(1923); cf. *C. A.* 17, 2031.—The purpose of this series of articles is to acquaint the reader with the actual methods used in the manuf. of the more important synthetic perfumes. Directions are given for the prepn. of pseudoionone by the condensation of the citral of lemon-grass oil with AcMe, and for the subsequent cyclization with H_2SO_4 to α - and β -ionone. Large-scale operations are described for the manuf. of methyl heptinecarboxylate and geranyl formate. W. O. E.

Manufacture of morphine from adulterated Indian opium and its waste products by the Robertson-Gregory process. JITENDRA NATH RAKSHIT. *J. Soc. Chem. Ind.* 42, 351-2T(1923).—The results obtained in a study of the conditions under which the max. yield of morphine may be effected from contaminated and waste products are given and the procedures followed are described in considerable detail. W. O. E.

Detection of esters of fixed acids in essential oils. A. RECLAIRE. *Perfumery Essent. Oil Record* 14, 293(1923).—It is shown by expt. that for practical purposes it is quite sufficient to acidify immediately after sapon. with H_3PO_4 and to distill off the liberated acids. The use of tartaric acid has no advantage. W. O. E.

Liquid synthetic menthol. ANON. *Perfumery Essent. Oil Record* 14, 294-5(1923).—Synthetic menthol is about 2.5-3 times more toxic than ordinary menthol. This is partly due to the fact that the synthetic prepn. is more volatile and probably also more readily absorbed by the tissues. External administration in usual amts. is harmless. Prolonged inhalation of the synthetic product is more poisonous than that of the ordinary menthol. Its antiseptic properties are also stronger, doubtless because of its higher toxicity. W. O. E.

Adulterated oil of bitter orange. AUFRECHT. *Pharm. Ztg.* 68, 614(1923).—A sample is described consisting apparently of a mixt. of bitter orange oil with oil of turpentine and the ester of a difficultly volatile acid. W. O. E.

Organic compounds of arsenic. R. F. HUNTER. *Chem. News* 127, 70-2, 82-4, 113-4(1923).—Beginning with the year 1760 when Cadet produced his "fuming liquid," a brief survey is given. W. O. E.

Disinfecting action of pyromucic acid. H. P. KAUFMANN. *Ber. pharm. Ges.* 33, 132-9(1923).—Exptl. data are presented showing the unsuitability of this acid as a preservative. W. O. E.

Constituents of some Indian essential oils. VIII. Essential oil from the gumoleo-resin of *Boswellia serrata* (Roxb.). J. L. SIMONSEN. *Indian Forest Records* 9, Part 6, 289-306(1923); cf. *C. A.* 17, 1299.—A careful examn. of the oil, first isolated and described by Pearson and Singh (cf. *C. A.* 13, 1528), shows the main constituents to be *d*- α -thujene, α -pinene and *d*- α -phellandrene in very small amts., while the higher fractions contain sesquiterpenes and their alics. W. O. E.

Production of synthetic camphor. S. P. SCHOTZ. *Chem. Age* (London) 9, 114-6(1923).—In addn. to discussing the 2 syntheses by Komppa, and by Perkin and Thorpe, more particularly the details in the production of camphor from pinene, S. shows how synthetic chemistry has within recent years deprived what used to be the only camphor-producing country in the world of a valuable monopoly. W. O. E.

Extraction of piperitone from essential oils. JOHN READ AND H. G. SMITH. *J. Soc. Chem. Ind.* 42, 339-40T(1923).—The ordinary process of fractional distn. under atm. pressure, in addn. to causing complete racemization and partial decompn. of the ketone, is ineffective in completely removing the associated substances, while extn. with Na_2SO_4 and $NaHSO_4$ solns. under the usual conditions is exceedingly tedious. By using a mechanically shaken, steam-jacketed vessel it has been found possible, however, to remedy the last-named defect and to ext. the piperitone in 80% yield, particularly by using Na_2SO_4 (1750 g. crystd. in 500 cc. H_2O , oil 1750 cc.) rather than $NaHSO_4$ in the process, 6 hrs. sufficing for the agitation. In order to prevent the mixt. from becoming alk., 5 successive quantities (90 cc.) of glacial AcOH are added at intervals during the extp. Various exptl. procedures are described for manipulating the addn. product. W. O. E.

Dextrinozol, the scent carrier of certain commercial dextrins; ozols in general. HERMANN KUNZ-KRAUSE. *Ber. pharm. Ges.* 33, 149-55(1923).—The term "ozole" is applied to certain volatile aromatic-narcotic odors or scents noticeable in com. dex-

trins and plant exts. On steam-distg. dextrin, crystals were obtained, which in form and melting point (53.75–54°) closely resembled myristic acid. From this and other expts. the conclusion is drawn that the "dextrin scent" of com. dextrins is due to a readily volatile solid constituent, dextrinazol, which in all probability is an ester, either of an unsatd. (convertible into a fatty acid) acid with possibly a terpene-related radical, or a fatty or higher constituted dicarboxylic acid with an alc. radical of the olefin, acetylene or terpene group.

W. O. E.

Variation statistics as help to pharmacognosy. L. ROSENTHALER. *Ber. pharm. Ges.* 33, 158–60(1923); cf. *C. A.* 16, 1483; 17, 850.—(X). *Fatty content of cacao nibs.* Of 3 sorts examd. (Acera, Ariba and Thomé) the maxima were found to fall in the groups 52–4, 50–2 and 48–50%, resp. (XI). *Oil content of plum pits.* The typical values fall between 39.56 and 49.42%.

W. O. E.

Essential oils in the leaves of *Librocedrus bidwillii*. B. H. GOUNDE. *J. Soc. Chem. Ind.* 42, 350–1T(1923).—The oil of *L. bidwillii* consists of (a) terpenes 30%, of which *d*-pinene is the chief constituent, and (b) sesquiterpenes 70%, which are strongly levorotatory and contain either cedrene or a new sesquiterpene.

W. O. E.

The making of medicines. E. F. COOK. *Am. J. Pharm.* 95, 581–98(1923).—Historical review.

W. G. GAESSLER

The status of insulin. ANON. *Am. J. Pharm.* 95, 368–78(1923); *J. Am. Med. Assoc.* 80, 1238–41.—A resumé.

W. G. GAESSLER

The chlorine antiseptics, with special reference to their pharmaceutical status. C. M. SMYTH, JR. *Am. J. Pharm.* 95, 232–6(1923).—A review including a brief description of Dakin soln., chloramine-T, and dichloramine-T, resp.

W. G. G.

Caffeine and sodium benzoate. A puzzle unravelled. J. ROSIN. *Am. J. Pharm.* 95, 224–6(1923).—With $\text{NaC}_7\text{H}_5\text{O}_2$ alone the U. S. P. method of assay is almost invariably several % low; with caffeine and $\text{NaC}_7\text{H}_5\text{O}_2$ the results are good and frequently a little over 100%. Correct results with $\text{NaC}_7\text{H}_5\text{O}_2$ alone are readily obtained by applying a modification suggested by Elvove. By this modification with caffeine and $\text{NaC}_7\text{H}_5\text{O}_2$ the results for $\text{NaC}_7\text{H}_5\text{O}_2$ are several % too high, the sum of the caffeine and $\text{NaC}_7\text{H}_5\text{O}_2$ in the moisture-free compd. amounting to 103% or even more. R. explains the abnormalities with the U. S. P. assay by the well known fact that when an alkali carbonate is ignited with nitrogenous matter, cyanide is formed. Although it generally yields about 0.5% lower values, the direct detn. of $\text{C}_6\text{H}_5\text{COOH}$ is preferred and the following procedure recommended: About 1 g. of the caffeine and $\text{NaC}_7\text{H}_5\text{O}_2$ previously dried to const. wt. is dissolved in 20 cc. of H_2O , 5 cc. of NaOH (test soln.) added the caffeine extd. with CHCl_3 , the CHCl_3 evapd. and the caffeine weighed. The aq. liquid is next treated with an excess of dil. H_2SO_4 , the liberated $\text{C}_6\text{H}_5\text{COOH}$ extd. with CHCl_3 , the CHCl_3 soln. evapd. at a very low temp. in an Erlenmeyer flask to a few cc. mixed with about 30–40 cc. of dil. alc. and titrated with 0.1 *N* alkali.

W. G. G.

The tannin of wild-cherry bark. JOSIAH C. AND BERTHA L. DE G. PEACOCK. *Am. J. Pharm.* 95, 613–23(1923).—Gallic acid is not present in wild-cherry bark. Cold water exts. but part of the tannin, for there is also a considerable proportion of cold-water-insol. phlobaphene. The tannin of this bark, as pointed out by Proctor (*Am. J. Pharm.* 1834) is an "iron-greening" tannin. This tannin yields a red phlobaphene by action of acids, including that of BzOH . There is a considerable proportion of free BzOH in this bark, the occurrence of which was first reported by Power and Moore (*C. A.* 3, 1529). The occurrence of BzH in living plant material may be taken as indication of possible presence of BzOH in any subsequently dried form of the part. The tannin is the bitter principle as well as the astringent constituent. The bitter principle, which is the tannin, is not the fluorescent principle. The free BzOH present decomposes the cold-water-sol. tannin with production of cloudiness or sediment in preps. of wild-cherry bark. This association of tannin and BzOH in the bark also explains the addn. of glycerol to the water used for extn. of the bark in the prepn. of the syrup.

W. G. GAESSLER

Chemical data on *Rapanea laetevirens*. E. H. DUCLOUX AND MAX AWSCHALOM. *Anal. soc. quim. Argentina* 11, 6–24(1923).—*Rapanea laetevirens*, fam. Myrsinaceae, is a large shrub native to Argentina. It is a favorite host of *Cerooplastes bergi* (cf. *C. A.* 17, 832). From the dry bark 0.809% of an acid saponin and 0.213% of a neutral saponin were isolated. Both saponins are glucosidic in character and possess very strong hemolytic properties. The bark contains no alkaloids or other compds. of interest.

L. E. GILSON

A new hypnotic of the barbituric series: butylethylmalonyl urea. P. CARNOT AND M. TIFFENBAU. *Compt. rend.* 175, 241–4(1922).—When they discovered veronal Fischer and von Mering studied only the sym. disubstituted malonylureas. C. and T.

have studied the unsym. derivs. obtained by replacing one of the Et groups of veronal by other radicals ranging from Me to C_7H_{15} . A table of data is given and the reports of the clinical and pharmacodynamic studies show that *butylethylmalonylurea*, m. 128°, sol. in 3 parts H_2O at 15°, is 3 times as hypnotic in its effect as veronal. O. B. H.

The manufacture and uses of chloramine-T. M. BRISCOE. *Chem. Age* (London) 9, 168-9(1923).

The analysis of some phenolic medicaments. EMILE LUCE. *Ann. fals.* 16, 293-8(1923).—The Codex method for detn. of PhOH and salol in gauzes (addn. of KBr and HCl and titration with standard NaOCl) is unsatisfactory and unreliable owing to indefiniteness of the end point. Koppeschaar's $KBrO_3$ method is recommended as follows: to 5-30 cc. of a 0.1% soln. of PhOH add 10 cc. of KBr (50 g. KBr to 150 cc.), 30 cc. of 95% alc., 5 cc. of 0.1 N $KBrO_3$ (16.70 g. per l.), and 10 cc. of 10% HCl. After 2 min. add 10 cc. of 10% KI and titrate with 0.1 N $Na_2S_2O_3$. The $HBrO_3$ should be standardized against the $Na_2S_2O_3$. 1 cc. 0.1 N $Na_2S_2O_3$ = 0.001566 g. PhOH. The CaH_2Br_2OH formed should be kept in soln. by addn. of sufficient alc., as on pptn. it occludes Br_2 . There should be a large excess of KBr to prevent loss of Br_2 by volatilization. The excess of Br_2 should be titrated promptly to prevent loss by the reaction $Br_2 + H_2O = 2HBr + O$. With 5-25 mg. of PhOH results were accurate to $\pm 1\%$. Salicylic acid on treatment with Br gives CaH_2Br_2OH , as also does salol after sapon., and they can be detd. like PhOH (after neutralizing with NaOH). 1 cc. 0.1 N $Na_2S_2O_3$ = 0.0023 g. salicylic acid and 0.001783 g. salol. α -Naphthol fixes 2 Br atoms and β -naphthol only 1. To det. them dissolve 0.20 g. in 10 cc. of 95% alc., add 20 cc. of N NaOH and make up to 100 cc., and proceed as with PhOH on a 10 cc. aliquot (preferably using starch indicator). With benzoic and salicylic esters of CaH_2OH dissolve 0.50 g. in 20 cc. of 95% alc., add 20 cc. of N NaOH and 10 cc. of H_2O , boil under a reflux condenser for 30 min., cool, make up to 250 cc., and proceed as before on a 20-5 cc. aliquot. 1 cc. of 0.1 N $Na_2S_2O_3$ = 0.0036 g. of α -naphthol, 0.0072 g. of β -naphthol, 0.124 g. of benzonaphthol, and 0.0033 g. of betol. Thymol fixes 2 atoms of Br with formation of dibromothymol, b.p. 158-60°, giving a Bz deriv. m. 88-9°, but no nitroso deriv. To det. dissolve 1 g. of pulverized thymol in 10 cc. of NaOH soln., make up to 1 l. with H_2O , and proceed as above on a 20 cc. aliquot. 1 cc. of 0.1 N $Na_2S_2O_3$ = 0.00375 g. thymol.

The analysis of sweet orange oil. F. BERTÉ. *Riv. ital. ess. profum.* 4, 110-2 (1922); *Chimie et industrie* 10, 115-6(1923).—Analysis of sweet orange oil offers certain difficulties owing to the presence of small amts. of easily substituted oxygenated substances. The most common adulteration consists in adding orange oil terpenes, which are now prepd. so well that they can easily be mistaken for natural oil of orange. A sample of these terpenes gave on analysis: d_{15} 0.8474, $[\alpha]_D^{20}$ 99° 40', $[\alpha]_D$ (on 50% distillate) 100° 10', difference 0° 30', residue on water bath 2.90%. These figures are very close to those for genuine oil of orange. Presence of over 1.5% of citral tends to show addn. of citral. Less than 1.5% citral indicates addn. of terpenes from orange oil. More than 2-3% residue at 100° indicates grease, resin, or mineral oil, etc. Analyses of pure oil, and of oil mixed 2% and with 4% of common oil gave, resp.: d_{15} 0.8490, 0.8505, 0.8502; $[\alpha]_D^{20}$ 99° 15', 97° 40', 96° 5'; $[\alpha]_D$ (on 50% distillate) 100° 45', 100° 25', 100° 20'; difference 1° 30', 2° 45', 4° 15'; residue on evapn. 2.4, 5.60, 7.26%; sapon. no. 194.4, 162.3, 175.5. Examn. of the residue on evapn. shows the nature of the fat or oil added. The oil contains 0.5-0.8% linalyl acetate. The important detns. are: organoleptic characteristics, d_{15} , $[\alpha]_D^{20}$, $[\alpha]_D$ on 50% distillate, b. p., citral content, residue on evapn., ester no., % of residue, soly. in alc.

Theriaca. GUSTAF DRAKE. *Svensk Farm. Tids.* 27, 375-80, 385-8(1923).—An historical study of the panacea, theriaca Andromachi.

A morphological and chemical study of *Nicandra physalodes* (L.) Pers. ANTON HOGSTAD, JR. *J. Am. Pharm. Assoc.* 12, 576-82(1923).—The material was grown from seed in S. Dak. The morphological characteristics are described. They agree with those reported by earlier observers. The leaves were assayed by the U. S. P. method for belladonna leaves and 0.1% total alkaloids found. The alkaloids had a tobacco-like odor but were not identified.

Constituents of peach leaves (KARIYONE, KIMURA) 11D. The action of As on protoplasm (VOEGTLIN) 11H.

The British Pharmaceutical Codex. London: Pharmaceutical Press. 30s. 9d. post-free. Reviewed in *Perfumery and Essential Oil Record* 14, 272(1923).

REUTTER, L.: *Traité de matière médicale et de chimie végétale*. VII and VIII (with index). Paris: Librairie J. B. Baillière et Fils. Reviewed in *Pharm. J.* 111, 61(1923). Cf. *C. A.* 17, 1691, 2347.

LAQUEUR, E., GREVENSTUK, A., SLUYTERS, A., AND WOLFF, L. K.: *Die neuern chemotherapeutischen Präparate aus der Chininreihe (Optochin, im besonderen Eukupin und Vuzin) und aus der Akridinreihe (Trypaflavin, Rivanol)*. Berlin: Julius Springer. 90 pp. Paper, 3s. Reviewed in *Chemistry & Industry* 42, 820(1923).

Ointments and lotions. I. RAHLIEFF. *Brit.* 193,024, Jan. 30, 1923. A lotion or ointment for external use (for rheumatism) is prepd. from enzymes of saprophytic bacteria. To obtain 100 g. of the lotion, cultures of the bacteria (*B. subtilis*, *Ididium albicans*, and *Staphylococcus*) are sterilized in 0.5% formalin and 25 g. of the prepn. are mixed with a 2nd prepn. This 2nd prepn. contains 70 g. of a neutral oil which with 0.3% of "ferum sesquichloratum" is heated to boiling and then cooled, mixed with 1.3% of pure BaSO₄ and again heated to boiling, then again allowed to cool and to remain for 24 hrs. at ordinary temp. The mixt. is again heated to boiling, 1.2% of Li₂CO₃ gradually added, the mixt. cooled to ordinary temp. and a soln. of 0.5% of Sr(NO₃)₂ in 5 g. of CHCl₃ is added. The 2 preps. are then mixed and kept at a const. temp. for 48 hrs. As a preservative 0.02 g. of "carboxyl metalloids" are added, and the lotion, which is bright yellow, may be colored green with neutral chlorophyll.

18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C. ZEISBERG

Sulfuric acid manufacture with truncated cone chambers. C. TIRALDI. *Giorn. chim. ind. applicata* 5, 163-5(1923).—The manuf. of H₂SO₄ by the Mills-Packard truncated cone chamber system differs from the usual method not only in the form of the chambers, but also in having external cooling by water. This results in greater cooling of the gas, and hence a greater production of H₂SO₄ per cu. m. The first cost is 1/4 less than that of the ordinary Pb chambers. Details of construction and working are given, also 3 photographs.

ROBERT S. POSMONTIER

Large sulfuric acid plants. LUIGI CANTIMORRI. *Giorn. chim. ind. applicata* 5, 166-7(1923).—The present cost of production of oleum in Italy is greater than that of chamber H₂SO₄. Hence many Pb chamber plants have arisen since the war. The application of the elec. purification of gases (Cottrell system) to oleum plants will bring about an important change in this state of things and result in lowering the cost of oleum.

ROBERT S. POSMONTIER

Fausser synthetic ammonia process. A. ZAMBIANCHI. *Giorn. chim. ind. applicata* 5, 171-6(1923).—Descriptive, with sketches and photographs. The topics considered are: production of H, synthesis of NH₃, oxidation of NH₃ and production of N, yield. Also in *Chem. Age* (N. Y.) 31, 413-5(1923).

ROBERT S. POSMONTIER

Synthetic ammonia by the Claude process. F. MEYER. *Z. angew. Chem.* 36, 404-5(1923).—An abstract of an article in *Chem. Met. Eng.*, translated from M. Lheure, *Mém. et compl. rend. travaux soc. ing. civils* 8, 326-33(1922); cf. *C. A.* 17, 1308.

F. C. Z.

Suggestions on the erection and supervision of electrical plants in potash works. F. BURGER. *Kali* 17, 97-103(1923).—A discussion on the elec. illumination of potash works and the causes and preventions of certain electric motor troubles peculiar to such places.

K. D. JACOB

Technical preparation of copper sulfate. T. MATSUNO. *J. Chem. Ind. Japan* 25, 926-30(1922).—Cu sulfate was prepd. on a large scale from roasted cement Cu contg. sol. Cu (expressed as CuO) 59.06, insol. Cu(Cu₂O) 2.58, sol. iron (FeO) 11.05, insol. iron (Fe₂O₃) 3.40, silicic acid 2.41, and O, etc., 21.50%. About 100 cu. ft. of warm water is poured into a dissolving tank (about 200 cu. ft. capacity), 8 lbs. of H₂SO₄ of 50° Bé. (sp. gr. 1.53) is added, and after agitation for 10 min., the calcd. quantity of Cu is introduced, the temp. of the bath being maintained at 60-80°. After 10 min., further quantities of the acid and Cu are added, and the process is repeated until about 1500 kg. of Cu has been added. The soln. is then transferred to an evap. bath by means of siphons and cood. to 34.5° Bé. (sp. gr. 1.314), then transferred to a crystg. tank, in which many lead plates are suspended for supporting the crystals. The crystn. is completed in

about 1 week. The product is collected, crushed, washed with water and dried at about 50°, the yield being about 1 ton. The extn. of Cu is more than 92%, and the product contains only 0.05% Fe and no other impurities. J. S. C. I.

Salt solutions and their graphic representation. FRITZ LAADE. *Kali* 17, 81-4, 103-7, 116-22, 137-40, 166-9, 197-202, 214-8, 230-4 (1923).—A general discussion with special reference to the graphic presentation of the relations existing between the various solid and liquid systems encountered in the formation, production, and purification of K, Mg, Na, and other salts from the German potash deposits. K. D. JACOB

Helium, a national asset. R. B. MOORE. *Trans. Am. Inst. Mining Met. Eng.* 1269M, 11 pp. (1923); cf. *C. A.* 17, 1111.—Utilizing the results of research in the lab. and with plants built on a semicommercial scale, the Government's production plant at Fort Worth yields He of 60-70% purity in the first step, and of 92-4% when reprocessed. The present plant is expected to make daily 30,000 to 40,000 cu. ft. of He 93-5% pure. A projected semi-commercial plant will be about 25 times the size of the above, and the final com. unit will be 10 times the size of the semi-commercial one. Two repurification units for gas contaminated through use in a balloon are under construction by the Bureau of Mines for the Army. One of these leads the gas through a liquefier surrounded by liquid air, and under the pressure on the gas and at the temp. obtained the N and O are liquefied while the He passes on in its original purity. In the other plant impure He is passed through a tube contg. charcoal at relatively low temps.; N and O are adsorbed while He passes on. Simultaneously one adsorber will be in use, several will be cooling down, and another will be out-gassed or heated, thus giving a continuous process yielding He of 99.9% purity. Plants for the Navy are also under way. As this country is the only one known to have large supplies of natural gas contg. He, it is inadvisable that any of the He be exported. By a proper distribution of 5 or 6 plants, it would be possible to ext. 50 or 60 million cu. ft. of He annually in the United States—or even 100 million cu. ft. in an emergency. But a proper system of conservation must be employed to prevent the waste of He-bearing natural gas; such as using gas from deeper sands first for com. purposes, leaving the gas from shallower sands, richer in He, for exploitation later. An account of the natural sources of He and theories as to its origin are given. W. C. EBAUGH

The uses of carbon dioxide. II. C. L. JONES. *Can. Chem. Met.* 7, 205-7 (1923); cf. *C. A.* 17, 2938.—The use of CO₂ at low pressure is classic in such processes as the LeBlanc, Claus-Chance, Solvay, sugar manuf., etc. CO₂ is used as a vehicle in the distn. of tar, petroleum, valuable org. chemicals, P compds., etc. As an antioxidant it is used in the extn. of logwood. In the Dutch white-lead process it is generated by fermenting manure or spent tan bark, while in the Carter process the CO₂ is produced separately by one of the usual methods. Liquid CO₂ is used in the manuf. of salicylic acid, and its use is suggested for the manuf. of urea during the slack winter season. As a cheap source of decentralized power, liquid CO₂ finds such uses as tin inflation, blowing out plugged water pipes, testing containers, etc., for leakage, driving torpedoes, spray printing, etc. For fire prevention and extinction CO₂ has advantages over steam and CCl₄. Its advantages over H₂O render it useful in protecting transformers, extinguishing fires in telephone switchboards, ship cargoes, coal piles, coal mines (treated in some detail), and preventing fires in oil tankers. Unlike foam extinguishers it cannot freeze. It is also used, to prevent dust explosions and to destroy vermin in stored grain. Its physiol. effects, both internal and external, are covered briefly. CO₂ finds application in the rubber industry as an antioxidant and by reason of its relatively high soly. in rubber. Addn. of CO₂ to the air of greenhouses to increase plant growth has recently been patented. Numerous references to the literature are given. E. G. R. ARDAGH

An attempt to cheapen the production of zirconium dioxide. J. W. BATY AND G. E. GOLLOP. *Can. Chem. Met.* 7, 35-8 (1923).—Brazilian zirkite runs 70 to 80% ZrO₂; only 55 to 65% of the Zr is actually present as ZrO₂; the remainder is silicate. In the Florida zirconia sands there is more Zr silicate and hence these sands are harder to treat. By passing dry Cl₂ or COCl₂ over heated Zr-bearing ore mixed with C, ZrCl₄ can be volatilized and pure ZrO₂ can be prepd. therefrom. The reaction is slow; the yields for Cl₂ are far from theoretical; and the process is difficult to carry out commercially. Fusions with (a) NaOH, (b) Na₂CO₃, (c) niter cake and (d) KHF₄ are described in *C. A.* 15, 3952. Of the soln. methods the best employs 66° Bé. H₂SO₄. By using 2 pts. H₂SO₄ to 1 pt. ore and heating to approx. 275° for 1 hr., 1-7% of the ZrO₂ in some Brazilian ore is brought to soln. Higher temps. and longer time did not increase the yield. The usual methods of producing a pure ZrO₂ from the H₂SO₄ soln. are too expensive for com. work. After extg. the residue with hot H₂O, the ZrO₂ can be pptd. by boiling as basic sulfate (Pugh's pat. U. S. 1,316,107). To reduce the free H₂SO₄ to approx. half

that of the ZrO_2 present, addn. of (1) $CaCO_3$, (2) $CaCl_2$ and (3) $CaCO_3 + CaCl_2$ were tried. B.'s and G.'s expts. show that Zr is retained by the pptd. $CaSO_4$, and that great diln. is necessary to bring down the ZrO_2 in appreciable amt. by boiling. By suitably adjusting the concns. and dilg. the filtrate about 40 times before boiling, about 75% of the ZrO_2 in soln. can be pptd. The ppt. merely requires washing and ignition. One sample so obtained gave on analysis 98.6% ZrO_2 . E. G. R. ARDAGH

Six types of carbon. J. N. A. SAUER. *Facts About Sugar* 17, 202(1923).—The various activated carbons now on the market are classified into 6 groups on a basis of the materials and procedures used in their manuf. T. SWANN HARDING

Gypsum and gypsum products. C. ELLIOTT. *Chem. Trade J.* 73, 245-8(1923).—The uses of gypsum are reviewed. E. H.

The importance and future of the German graphite output. E. H. SCHULTZ. *Chem.-Ztg.* 685(1923); cf. *C. A.* 17, 3074.—The Bavarian graphite production increased from 4,000 tons in 1907 to 36,000 tons in 1918, while the Austrian production fell from 50,000 to 32,000 tons, and that of Ceylon from 35,000 to 22,000 tons during the same period. Between 1891 and 1913 German imports rose from 13,000 to 44,000 tons. Because of excellent methods of treatment it is claimed that the local (German) varieties of prepd. graphite are superior to those obtained from other sources, chiefly because they come in flakes rather than in powder form. W. C. EBAUGH

Distillation of NH_4 from limed and carbonated beet juice and its influence on the composition of this juice (KOHN) 28. Quantitative decomposition of native fluorspar by fusion with excess of Na_2CO_3 (PALIT) 6.

Ammonia or hydrocyanic acid. AKTIEBOLAGET KVAEVEINDUSTRI. Swed. 52,047, June 28, 1922. N is absorbed in mixts. of C and alkali or alk. earth metals or compds. of these metals, eventually in the presence of Fe, Mn or other metals or compds. of these metals. H_2O vapor, or moist CO_2 , is applied during the absorption without removing the reaction mass. To replace the C consumed by the reaction an oxide of C, for instance CO, is introduced into the reaction chamber. It is decompd. into C which remains in the mass and other compds. which are removed. Consequently no addn. of solid matters is required during the working.

Absorption of nitrogen in mixtures of carbon and alkalies, etc. AKTIEBOLAGET KVAEVEINDUSTRI. Swed. 52,687, Nov. 15, 1922. Cf. Swed. 52,047 (above). The reaction mixt. is transformed into spherical or semi-spherical grains with a hardness of 2 or more (according to the hardness-scale of Mohr) before being fed into the reaction furnace.

Ammonium salts. E. B. BERGDAL. Swed. 52,046, June 28, 1922. Sulfate, carbonate or carbamide of NH_4 is formed by heating under pressure a mixt. of pure N_2 and H_2O vapor with metalloids such as S, P, or C or suitable oxides of these elements.

Basic aluminium sulfate low in iron. S. H. HULTMAN and A. R. LINDBLAD. Swed. 53,134, Dec. 6, 1922. To a soln. of neutral Al sulfate is added a hydroxide, carbonate or sulfide of an alkali metal or NH_4 in amt. insufficient for pptn. but sufficient to form a semi-insol. basic Al sulfate. The soln. is then heated in a closed vessel at increased pressure, by which a heavy sol. basic Al sulfate of the approx. compn. $Al_2O_3 \cdot 1.5SO_3$ and low in Fe is pptd., while the main part of the Fe is retained in the mother liquor.

Basic aluminium sulfate low in iron. A. R. LINDBLAD and S. H. HULTMAN. Swed. 53,132, Dec. 6, 1922. Normal, Fe-contg. Al sulfate is dissolved in water and heated with a salt of another acid than H_2SO_4 , the negative radical of which forms a sol. Fe salt. The process is carried out in a closed vessel at increased pressure. A basic Al sulfate low in Fe is pptd. immediately or just after cooling, while the main part of the Fe is retained in the mother liquor.

Removing iron from basic aluminium sulfate. A. R. LINDBLAD and S. H. HULTMAN. Swed. 53,133, Dec. 6, 1922. Basic Al sulfate of the approx. compn. $Al_2O_3 \cdot SO_3$ is heated with a soln. of another acid than H_2SO_4 , which acid forms a sol. Fe salt, or with a soln. of a salt of such an acid.

Aluminium sulfide. T. R. HAGLUND. Swed. 54,107, Mar. 28, 1923. Materials contg. Al_2O_3 are heated in an elec. arc with reducing agents such as coal or carbides (Al_4C_3) and one or more S compds. The gases from the arc are forced through a layer of the charged materials.

Aluminium sulfide. T. R. HAGLUND, O. MAGNUSSEN and H. LUNDIN. Swed. 53,941, Mar. 7, 1923. S or its compds., eventually with addn. of coal, is brought into reaction with one or more compds. of Al, such as Al carbides, Al_2O_3 , clay, bauxite, etc.

Mercuric chloride. I. V. DELMAR. Swed. 50,918, May 19, 1922. Hg is dropped through an atm. of Cl under reduced pressure into a liquid which does not absorb Cl at all, or only to a very small degree, and the temp. of which is kept just below the b. p. by addn. of further quantities of cold liquid.

Cyanogen compounds. AA. ESBJOERNSSON and O. TROLL. Swed. 51,803, May 31, 1922. N of suitable purity is made to react with C and alkali or alk. earth metals or oxides, hydroxides, carbonates, sulfides or sulfates of these metals in the presence or absence of catalysts. The reaction mass is divided into several units. The N and the reaction gas mixt. pass alternately through these units and through heating elements arranged between the units. The gas reaches in each of these elements a temp. above the reaction temp. The excess heat is utilized by the reaction in the next unit in each case to heat the reaction mass.

Treating materials containing phosphates. F. LILJENROTH. Swed. 51,749, May 24, 1922. The material is elutriated with phosphoric acid and the liquid is sepd. from the insol. residue. The H_2PO_4 is regenerated by pptg. the dissolved Ca with H_2SO_4 and is partly used for treating further quantities of the materials, while the excess is utilized as such or for the production of sol. phosphates.

Chromium compounds. A. R. LINDBLAD. Swed. 51,689, May 17, 1922. Finely ground ferro-Cr or another Cr alloy is mixed with a finely ground alkali or alk. earth metal or oxides or hydroxides of these metals and roasted in the presence of air or other oxidizing gases.

Evaporating and crystallizing strongly incrusting solutions. AKTIEBOLAGET GRAAEN. Swed. 53,821, Feb. 21, 1923. The soln. is evapd. in a long, narrow, outwardly heated rotary pipe and coincidentally cooled by blowing air through the pipe.

Pure carbon. AKTIEBOLAGET KVAEFFVRINDUSTRI. Swed. 52,048, June 28, 1922. CO is decompd. into CO_2 and C in the presence of Fe. The reaction is carried out at increased pressure and a suitable quantity of H_2 is added to avoid oxidation of the Fe.

Nickel catalyst. AKTIEBOLAGET HENRIKSBOGS FABRIKKER. Swed. 53,520, Jan. 24, 1923. $NiCO_3$ in the dry state is heated so long to 200–300° and treated so long with reducing gases that the carbonate on the surface of the particles is reduced to Ni while the central nuclei remain intact.

Removing oxygen from nitrogenous gas mixtures. C. T. THORSSELL and H. L. R. LUNDÉN. Swed. 51,932, June 14, 1922. The O is absorbed by an active substance, such as Fe. The temp. conditions are regulated in such a way that the heat set free by the absorption of O_2 is utilized for the regeneration of the absorbent, any considerable application of additional heat being thus avoided.

Polishing material. C. GRANFELT. Swed. 54,257, Apr. 11, 1923. An intimate mixt. of alc., turpentine, polishing oil and H_2SO_4 .

19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

Sir William Crookes' anti-glare glasses. J. H. GARDINER. *Chem. News* 127, 97–8(1923).

Variation in refractive index near the surface of glass melts. F. TWYMAN AND

A. J. DALLADY. *Trans. Optical Soc. (London)* 23, 13(1922).

Present day glass furnaces. TRIQUET. *Technique moderne* 15, 508(1923).—

A description with hints as to possible improvements. A. PAPINEAU-COUTURE

The application of research to plant problems in the ceramic industry. P. C. KINGSBURY. *Ind. Eng. Chem.* 15, 898–9(1923).

Ceramic products in the service of industry and commerce. W. TREPTOW. *Z. Ver. deut. Ing.* 67, 581–4(1923).—Various types of ceramic products are suited to the many different requirements of industrial processes. Many of these products and their uses are described.

Ceramic products as industrial materials. F. SINGER. *Z. Ver. deut. Ing.* 67, 584–6(1923).—A very comprehensive table is given listing all the phys. properties of a great variety of ceramic materials including building materials, refractories, stonewares, porcelains, silexite, fused quartz and the common metals.

The rational study of furnaces in ceramics. P. FRION. *Ceramique* 25, 1, 158–66; *Chem. Zentr.* 1922, IV, 489.—A discussion of the possibilities of better utilization of fuels. Further economy can be obtained by lower draft with poor coals, coal dust and

oil, preliminary gasification of the fuel, a spherical form for and extension of the combustion chamber and complete heat insulation and recovery. C. C. DAVIS

Materials for ceramic industry in Dutch East Indies. E. C. JUL. MOHR. *Ber. Af'd. Handelsmuseum Koloniaal Inst.* No. 14, 12 pp. (1923).—Samples of "Sawah Locotah" clay, quartz, kaolin and limestone were exam'd. in pottery factories. Yellow ware prepd. from these materials was satisfactory. One sample contg. 96.5% pure kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) with 0.183% Fe_2O_3 is equiv. to the best grades of English or Bohemian china clay and is perfectly adapted for use in the *paper industry*. VAN DER HOEVEN

The draft in rotary kilns. A. HEISER. *Tonind. Ztg.* 47, 492 (1923). H. G. S. Specifications for building and sand-lime brick in Austria. ANON. *Tonind. Ztg.* 47, 492-3 (1923). H. G. SCHURECHT

Report of Refractory Materials Committee. Jointing materials for silica refractories. D. JONES AND W. EMERY. *Gas J.* 163, 157-9 (1923); *Gas World* 78, 646; cf. C. A. 16, 2770.—The more nearly a jointing cement approaches in chem. compn. and phys. behavior that of the bricks with which it is used, the more satisfactory are the results obtained. Examn. was made of the effect of mixing in various proportions, fireclay, ganister and crushed silica brick, and, in some cases, of adding plaster, lime and Na_2SiO_3 . Mixts. of the 3 first materials, having either equal or greater proportions of ganister to crushed silica brick, give very good jointings. A high % of the latter renders the cement mechanically weak. For the bonding material, a small % of a highly plastic refractory clay is more satisfactory than a large proportion of fireclay of a less plastic nature. No advantage is obtained by the addn. of such materials as plaster, lime or Na_2SiO_3 to a cement which is to be used at high temps. J. L. WILBY

Furnace settings and refractory cements. F. J. WAKEM. *Ind. Eng. Chem.* 15, 893-4 (1923).—A general discussion of failures due to plastic deformation, spawling, cracking or bulging, clinkering, melting and slagging. A dry, high-temp. cement is preferable to a plastic cement. Excess of H_2O should be avoided. C. H. KERR

Vitreous enameling in the electric furnace. J. L. MCK. YARDLEY. *Elec. World* 82, 327; *Chem. Met. Eng.* 29, 55-8 (1923).—Recent furnace improvements include carborundum or carbofrax brick muffle, intermittent gas fire and elec. heat. Carborundum has $\frac{1}{4}$ the thermal resistance of fireclay. In the intermittent furnace, gas is burned directly in the chambers and heated above the required temp. Then the gas is turned off and the enamel is fused under falling temp. With 500 B. t. u. gas at 50 cents the fuel cost with intermittent gas furnace is 9 cents per 100 lbs. or 10 cents per 100 sq. ft. of surface. Cost in elec. furnace will be as low if power cost is 1 cent per kw.-hr. Furnaces for watch dials, bath tubs and sheet Fe are described and other cost data given. R. J. MONTGOMERY

Glass-to-metal joint (MEYERS) 1. Sealing base metals through glass (HOUSKEEPER) 1. Evaporation of water from clay (FISHER) 13.

20—CEMENT AND OTHER BUILDING MATERIALS

J. C. WITT

The French "fused cement (electric)." NITZSCH. *Zement* 12, 142-3 (1923).—A tabulation and comparison of the analytical results and phys. properties of "fused cement" obtained by different investigators. R. F. SCHNEIDER

The most economical size of treating plant retort. GRANT SHIPLEY. *Railway Age* 74, 1002-3; *Wood Preserving News* 1, 130-1 (1923).—Most treating retorts are provided with narrow gage tracks for carrying the trams. A standard gage track for this purpose permits of more economic handling of the material to be treated. For a retort designed to carry standard gage tracks a cylinder diam. of 90 to 96 in. is recommended as the most economical. ALFRED L. KAMMERER

Experimental researches on the electrical treatment of wood in Italy. L. PETRI. *Ann. r. Inst. superiore forestale Naz.* 7, 3-118 (1921); *Bull. Agr. Intelligence* 12, 1431-4.—An exhaustive summary of the present knowledge regarding electro-capillary phenomena is given followed by a description of the exptl. attempts made in the past to dry and preserve wood by elec. treatment. P.'s lab. expts. demonstrate that impregnation of wood with solns. of electrolytes and the passage of elec. currents involves two classes of phenomena, viz., electroosmosis and the movement of the ions. Electroosmosis is only of importance when it is desired to obtain an appreciable exosmosis of the wood sap. The amt. of liquid carried through the wood in a unit time varies with the species, the

concn. and cond. of the sol and the current density. Liquids having a relatively high dielectric const. give the best impregnation. As a rule a. c. is preferable to direct. Complete impregnation can be obtained only in green or fresh ligneous tissue. Elec. impregnation fixes in the tissue certain metallic salts, e. g., ZnCl_2 , thus preventing subsequent leaching by water. The seasoning of wood by electricity is not practical as the high voltage required reduces its strength. The preservative substances likely to give good results are ZnCl_2 , HgCl_2 and CuSO_4 , if a low frequency a. c. of not more than 0.5 amp. per sq. dm. is used.

ALFRED L. KAMMERER

Results of antiseptic treatment of sleepers. R. S. PEARSON. *Indian Forest Records* 9, part 1, 49 pp. (1922); cf. C. A. 13, 504.—A record of durability tests of treated railway ties made from native woods and laid in tracks in various climatically different parts of India. Five species of wood not naturally resistant to decay and white ant attack were treated in 1909-1911, the four following non-pressure treatments being employed: Powellizing (As salts and sugar residues); carbolineum; ZnCl_2 soln. followed by creosote oil; mixts. of creosote oil and crude petroleum. The latter mixts. were also injected by pressure. The test further included ties of Indian woods treated in England by the full cell process with creosote oil and 200 Douglas fir ties treated in America. The results after ten years indicate that the choice of treatment lies between (1) the full cell process using either straight creosote oil or creosote and petroleum combined or (2) Powellizing, cost being the governing factor. Further expts. using the Rueping and the Card processes are advocated. It is demonstrated that for the best results the treated ties should be laid heart side up, not down as practiced generally.

ALFRED L. KAMMERER

Zinc chloride as a timber preservative on the Chicago, Milwaukee and St. Paul Railway. P. S. POOLER. *Wood Preserving News* 1, 111-2 (1923).—Four test track sections laid with ZnCl_2 -treated ties were installed on the C. M. & St. P. Rwy. in the years 1903, 1906 and 1911. Of the 1903 ties 98% of the untreated white oaks have been removed with an av. life of 12 years while 57% of the Zn-treated pine ties are still in good condition. Of the treated red oak ties laid in 1906, 85% are still in the track. Of the 1911 treated beech ties, 42% have been renewed. In the Hartford, Wis. test track 90 to 96% of the untreated red oak and maple ties have been removed whereas 94 to 100% of the Zn-treated ties of the same species are still in good condition.

ALFRED L. KAMMERER

Rubber-surfaced articles (Brit. pat. 193,137) 30.

Cements. H. KONTZLER. Brit. 193,372, Aug. 1, 1922. Slow-setting cements are produced by the fine pulverization of an intimate mixt. of gypsum with aluminates, hydroxides of Al_2O_3 such as bauxite, or natural or artificial puzzuolanas, e. g., blast furnace slag. In the case of a slag contg. less than 30% of SiO_2 and more than 10% of Al_2O_3 , 16-20% of gypsum, previously dried at 80° , is used.

Treating cement kiln dust. PATENTAKTIEBOLAGET JUNGNERNS KALI-CEMENT. Swed. 52,582, Aug. 30, 1922. The dust is treated with nitrous gases or HNO_3 in order to transform the alkalis into a water-sol. state and the CaO compds. into $\text{Ca}(\text{NO}_3)_2$.

Manufacture of cement, burned lime, etc., in electric furnace. T. A. F. HOLMGREN. Swed. 59,536, Jan. 4, 1922. The raw materials are crushed into suitable grain sizes, mixed and fed into an elec. furnace. The heat is produced in one or more zones by a. c. which is applied through one or more circuits with phase-differences like 360° divided by the no. of circuits. Gas is drawn or forced through the furnace in opposite direction of the materials.

Acid-proof mortar. E. S. QVIDINGER. Swed. 52,765, Sept. 20, 1922. An intimate mixt. of cement with finely pulverized chamotte and alum-slate is stirred with a suitable quantity of a soln. of alkali silicate of convenient concn.

Waterproof concrete. A. G. LINDÉN. Swed. 52,563, Aug. 23, 1922. A mixt. of 70-30 parts of cement and 30-70 parts of pulverized bricks or talc.

Treating slag bricks. AKTIEBOLAGET ARCUS BETONGINDUSTRI. Swed. 53,126, Nov. 29, 1922. The freshly formed bricks are subjected to steam or steam jets to bring about a preliminary binding before the hardening in the air.

Bricks and insulating stones. C. P. AASTROEM. Swed. 50,731 and 50,732, Jan. 18, 1922. A certain species of calcareous earth called "bleke" (found on the isle of Gothland in the Baltic) is passed through a fine-meshed screen, dried in the air and ground finely and then mixed with a binding substance. The latter is formed by mixing burned, sandy ground "bleke" with ordinary cement. Then water is added

and the mass is worked and pressed to blocks of suitable sizes and shapes, which are finally dried and hardened in the air. (Cf. 2 following abstr.)

Insulating composition. C. P. AASTROEM. Swed. 50,733, Jan. 18, 1922. The material "bleke" (cf. above) is screened, dried and finely ground and mixed with glue water to a thick paste, which is dried and ground very finely. It is then mixed with burned, ground "bleke," clay, cement and coir.

Porous insulating material. T. A. EKLUND AND C. G. LOEFVEBERG. Swed. 51,192, Mar. 8, 1922. A porous insulating material is formed by mixing "bleke" (cf. above) with cellulose. The cellulose may be partly replaced by other fibrous materials from which the incrusting substances are not removed, for instance peat fiber, peat dust, algae, straw, wood pulp, etc.

Building material. O. E. N. PETTERSON. Swed. 51,981, Aug. 16, 1922. Peat dust, slaked lime and linseed cake stirred in water are mixed to a pasty mass which is pressed into molds and dried.

Protecting buildings against corrosive liquids. P. G. EKSTROEM. Swed. 51,521, Apr. 26, 1922. Those parts which are likely to be subjected to corrosion are coated with gypsum, with addn. of an inactive substance, for instance SiO_2 .

21—FUELS, GAS, TAR AND COKE

A. C. FIELDNER

Yield and quality of the gas, oil and other by-products of the constituents of the Freeport coal bed, Pa. J. D. DAVIS AND H. G. BERGER. Carnegie Inst. Tech. Co-operative Mining Courses, *Bull.* 1 (1922).—Thick Freeport coal when carbonized at temps. around 600° yielded 25-30 gallons of tar, 8000 cu. ft. of gas, 1380 lbs. of coke and 15-20 lbs. of $(\text{NH}_4)_2\text{SO}_4$. The tar yielded 38-42% oils b. up to 275°, 25-32% b₂₀ up to 300°, 23.5-37.5% soft pitch. Cannel coals gave 74.7-78.2% non-fused residue, contg. 35% ash, 27.5-33.5 gal. tar, and 3,800-4,500 cu. ft. gas per ton. The tar analyzed 35.8-44.2% oil, 48.4 and 26.7% vacuum oils, and 15.8 to 29.1% pitch. Bone coals yielded 78.2-79.5% semi-fused residue contg. 50% ash, 13-14 gals. of tar, and 3,400-3,600 cu. ft. of gas per ton. By-products from coals of this seam show definite variation in character with variation in microstructure of the coals.

Elimination of smoke by blowing steam over the grate. DELORME. *Technique moderne* 15, 508(1923).—Blowing steam by means of perfectly adjusted app. and for the time strictly necessary to prevent smoke causes a slight economy in fuel; but great care is required to prevent waste of steam, which would easily turn the saving into a loss.

The gasification of solid fuels. CH. COLOMBI. *Technique moderne* 15, 498-501 (1923).—Brief review of some recent patents.

How sulfur in fuel affects flue-gas composition. C. H. BERRY. *Power* 58, 95-6, 113-5(1923).—A table is given showing the relation between % of SO_2 in flue gas and % S in coal. The effect of S on ordinary methods of gas analysis and computation is small and except in refined tests may be neglected.

Thermal fractionation of the gases from carbonization of solid fuels. P. LEBEAU. *Compt. rend.* 177, 319-22(1923).—Gram samples of oak wood, pine wood, peat, lignite, fat and lean coals and anthracite were heated in a silica tube connected with a glass condenser surrounded by solid CO_2 and acetone. A Hg pump served to evacuate the app. and to remove the gases. A sample was exhausted at 100°, than at 200°, 300°, etc. Curves plotting m.³ of total gas per ton against temp. are given, but no results of analyses of the gases. Curves for anthracite and lignite resemble that for oak with maxima at 800°, while those for the coals and peat resemble that for pine with maxima at 600-700°. L. thinks these resemblances may bear a relation to a particular geological characteristic of a group of fuels and that this procedure for fractionating the carbonization gases might add to our knowledge of the origin and properties of solid fuels.

Adler and Hentzen—firing device for the power plant. PRADEL. *Chem.-Zig.* 47, 593-5(1923).—For the use of such fuels as brown coal, briquets, and peat which tend to pack on the grate and cannot be burned efficiently, a mech. feeding and grate turning device has been developed. The feeding device throws the fuel on the fire in such a way that it spreads in an even layer. A special grate is shown which permits the ready removal of ashes and clinkers. This latter device causes the loss of some unburned fuel, which must be sepd. from the ash. Illustrations of the various parts of the app. are given.

C. T. WHITE

Economy in the boiler room. E. HACK. *Chem.-Ztg.* 47, 639-41(1923).—The conditions for the economical burning of various fuels are given. Typical problems are worked out which show the loss in efficiency due to the use of too large an excess of air, and the heat lost in the flue gases. In general the firing of wood, peat, and brown coal may be best carried out with twice the theoretical amt. of air, gas coal with 1.75 times the theory, anthracite and coke with 1.4 times the theory. Good boiler room practice requires 13-14% CO_2 in the flue gas.

C. T. WHITE

The use of alcohol in explosion motors. "Eterol." A. PURGOTTI AND L. PURGOTTI. *Ann. scuola agr. Portici* [2] 16, 1-23(1920).—"Eterol" is a conventional name given to alc., suitably etherized and subjected to a special treatment (not divulged) for rendering it capable of replacing gasoline in explosion motors. Having a const. chem. compn. (not given), const. definite results are always obtained after the carburetor is once adjusted. The results of expts. in which it was used in automobiles are reported and the advantages of its use enumerated.

ALBERT R. MERZ

A contribution to the theory of internal-combustion motors. MARCUS BRUTZKUS. *Compt. rend.* 176, 1621-3(1923).—A discussion is given of the effect of variations in pressure, concn, and temp. on combustion. From the standpoint of rapidity and completeness of reaction, it is preferable to burn a motor fuel during compression if when burned under continuously increasing pressure an increase in the no. of mols. takes place. Conversely it is best to burn a fuel during expansion which when burned undergoes an increase in the no. of mols. under decreasing pressure. For fuels which burn without variation in the no. of mols., variation of pressure is without effect. The most satisfactory fuels are those in which the variation in the no. of mols. is greatest during the combustion as evidenced by the fact that CH_4 and ethylene in which the no. of mols. does not change and C_2H_6 and naphthalene in which the no. of mols. varies very little burn in a motor with difficulty. The introduction of an excess of air, followed by an increase in vol., favors the process of combustion in case of an increase, or invariability in the no. of mols. during combustion, and in the case of the diminution in the no. of mols. during combustion this influence is subordinated in a quant. ratio. Combustion in a motor is carried out under continually cooling influences, due to the vapor not being entirely burned during the explosion, by the walls, and in the const. pressure motors, by the evapn. of fuel gradually introduced, and by the expansion of the vapor. The reaction may be conducted in the direction and with the velocity desired by a continual exterior change of the pressure, temp. and concn., in the opposite direction to that caused by the reaction.

C. T. WHITE

Detection and estimation of spirits in benzene. P. SCHWARZ. *Chem.-Ztg.* 47, 462(1923).—In the attempt to remove alc. from benzene by washing with water, a stubborn emulsion was formed which could not readily be broken. Benzene was mixed with about an equal vol. of spindle oil, viscosity 2-50, a moderately concd. NaCl soln. was added and the mixt. shaken out in a separatory funnel, when an immediate sepn. of the liquids took place. The aq. portion was subjected to fractional distn. and the alc. was estd. in the distillate in the usual way. The analysis of mixts. of benzene and petroleum products depends on the nature of the petroleum substances present. The subject is discussed with reference to the work of Pritzker and Jungkunz (cf. C. A. 17, 2188) also with reference to the compn. of mixts. of benzene and petroleum used for motor fuel and for other purposes.

L. W. RIGGS

Piedmontese peats. T. SOLA. *Staz. sper. agrar. ital.* 55, 29-33(1922).—Analyses (showing ash, nitrogenous substance, fat (ether ext.), cellulose, humic substances, S, and calorific value) are reported for 9 peats. The % of ash varies from 10.94 to 41.94%. In consequence, the calorific power varies widely (4850 cal. for the 10.94% ash sample to 2763 cal. for the 41.94% ash sample). The % S is relatively low so no trouble should be experienced by reason of hastened deterioration of equipment. The nitrogenous substances are relatively high so that these peats are well adapted for the *prepn.* of $(\text{NH}_4)_2\text{SO}_4$. The % cellulose is also high so that the possible use of the material for the *manuf. of paper* should be investigated.

ALBERT R. MERZ

The liquefaction of coal. DAVID BROWNLEE. *Chem. Trade J.* 73, 248-9(1923).—A description of the Bergius hydrogenation process.

E. H.

Carbonization of coal by the coalite process. C. H. S. TUPHOLME. *Chem. Met. Eng.* 29, 233-8(1923).—An illustrated description of the plant at Barnsley. This consists of one unit of 20 retorts, each 9.5 ft. \times 7.5 ft. \times 11 in. and heated by Mond gas or by gas from the retort. Two perforated collapsible plates, 9.5 ft. \times 6 ft. 5 in., of hard Mn cast iron are supported 4 in. apart in the middle of the retort. The coal is carbonized in 2 slabs, 9.5 ft. \times 6.5 ft. \times 3.5 in., between the walls of the retort and these plates. The charge of 1344 lbs. is carbonized in 8 hrs. The temp. is 1200° F. outside and 1000°

F. inside the retort. In discharging, the iron plates are brought together and a rotary valve at the bottom is opened. The hot coalite drops into a water-jacketed iron cooler. The charge consists of a washed mixt. of 70% non-coking slack and 30% coking slack. Analyses on a dry basis of the non-coking slack, coking slack and coalite are, resp.: volatile matter 34.0, 36.4, 10.0; ash 4.9, 5.1, 6.4. Yields per ton are: 6000-6500 cu. ft. of 700-80 B. t. u. gas, 20 gals. of coalite oil giving 3 gals. motor spirit, 8-9 gals. Diesel or fuel oil and 8-9 gals. lubricating oil, 15 lbs. of $(\text{NH}_4)_2\text{SO}_4$ and 14 cwts. of coalite. The coalite finds a ready market as domestic fuel. Hence the use of the plant at pit heads to convert waste coal and breeze into solid fuel seems ideal. J. J. MORGAN

Combustibility of coal. A. KOREVAAR. *Stahl. u. Eisen* 43, 431-5(1923).—A recapitulation of K.'s theory of combustion in gas producers (cf. C. A. 16, 3200). Combustibility and rate of combustion must be distinguished. Comparative figures for the former may be obtained by burning the samples under const. conditions of furnace and air and comparing the max. temps. obtained in the "neutral plane" of the zone of combustion. Alternatively, the samples may be burnt in a shaft furnace of variable height in which the height of the fuel column is adjusted so as exactly to coincide with that of the zone of combustion. This is effected by increasing the height of the fuel column until the flame of burning CO reaches a max. The greater the combustibility of the fuel, the higher the temp. obtained and the smaller the zone of combustion. Koppers' test (cf. C. A. 16, 2289), in which fuel columns of equal heights are burned and the lengths of the CO flames compared, is given a new interpretation. A short flame does not mean that the fuel is incapable of effecting the complete reduction of CO_2 , but that the height of the fuel column employed is less than that of the zone of complete combustion. So long as the former is greater than the latter the length of flame obtained will be const. and independent of the combustibility of the fuel. J. S. C. I.

Caking-power curves of coal. A. BADARAU AND F. V. TIDESWELL. *Fuel* 2, 61-5 (1923).—The coking properties of a coal cannot be estd. completely by knowing either the compn. of the mixt. of coal and inert material that will just yield a coherent coke (cf. Gray, C. A. 17, 2040) or the strength of the coke produced from the coal alone (cf. C. A. 11, 2402). Various coals (60-mesh) were mixed with different proportions of electrode-C (60-90 mesh) and heated 7 min. at 900°. The crushing strengths of the buttons were plotted against the ratio, C/coal. These caking-power curves showed that the relative values detd. in the ordinary way by admixt. with inert material depended on the limiting crushing strength adopted. The coals could be grouped in 2 classes, 1 having a high initial coking strength which decreased rapidly on addn. of inert material, and the other a low initial coking strength which increased on addn. of inert material and then gradually decreased. The 1st class was distinguished from the 2nd by a higher O content. The strength of a coke is probably chiefly detd. by the strength of the carbonized cementing material (provided that sufficient is present but not an excess, which would reduce the strength). The amt. of inert material possible to add to a coal, and not prevent the formation of a coherent coke, is dependent on the amt., covering power and strength of the cementing material. C. C. DAVIS

Producer gas practice. H. STERN. *Chem. Eng. Mining Rev.* 14, 427-9; 15, 33-5, 74-8, 108-10, 154-7(1923).—A general paper. E. J. C.

Composition of Japanese natural gas. T. OHNO. *J. Chem. Ind. Japan* 25, 783-8 (1922).—Samples of natural gas from Haneda-machi (Tokyo prefecture), Moharamachi and Tsuchimutsumura (Chiba Prefecture), Niitsu oil-field, and Nuttari petroleum refinery gave the following results on analysis: CO_2 1.2-14.9, C_2H_6 0-0.1, O_2 0.2-0.7, CO 0-0.2, CH_4 79.1-92.1, N 4.6-11.3%; sp. gr. 0.577-0.725, calorific value 7023-844 g.-cals. per l. A sample from Nishiyama oil-field (Niigata Prefecture) proved to be a natural petroleum gas and gave the following results: CO_2 0.2-0.5, C_2H_6 0.7-1.0, O_2 0.5-0.6, CO 0.4, CH_4 22.8-44.0, C_3H_8 54.2-71.3% (satd. hydrocarbons were calcd. as CH_4 and C_2H_6), sp. gr. 0.807-0.963, calorific value 13,090-13,293 g.-cals. per l. J. S. C. I.

Chemical and thermal changes in heating gases for open-hearth furnaces during preheating, especially in the presence of tar vapors. E. MAURER AND S. SCHLEICHER. *Mitt. Kaiser Wilhelm Inst. Eisenforsch.* 3, 57-76(1922).—Expts. were carried out on gases contg. tar (from lignite briquets) and gases free from tar (from blast furnaces and coke ovens). Two formulas were deduced, expressing the changes in the gases from their introduction until they reached the top of the furnace. The exothermic reactions taking place and the deposition of C through dissoc. were adduced as causes of the fall of calorific value of the gases on heating. The presence of steam indirectly prevents this fall, as it causes the deposited C again to be converted into gas. The combustion of the deposited C is most difficult to effect in the case of coke-oven gas. J. S. C. I.

In burning carbon which is formed first, carbon monoxide or carbon dioxide?

CARL KULLBERG. *Teknisk Tids.* 53 (Kemi) 41-6(1923).—Coke was heated in a current of air under proper exptl. control and the CO and CO₂ were detd. Both CO and CO₂ were formed directly from the C and neither one can be considered as primary with respect to the other. The relative amts. depend upon the temp. With an increase in the temp. there was a relative increase in the CO₂. For 360° the figures reported indicate that there was 1 part CO to 4 parts CO₂. The burning of the CO to CO₂ is a relatively slow reaction and in the course of the expt. (360° series) only about 10% of the CO formed was oxidized. This work is in reply to the theories of Aufhäuser at present debated in the German journals. (Cf. book reference under A. in C. A. 16, 1311.)

A. R. ROSR

Estimation of the aromatic and unsaturated constituents of low-temperature tar. H. ARNOLD. *Z. angew. Chem.* 36, 266-7(1923).—It is especially difficult to isolate individual substances from low-temp. tar. The next best method is to isolate the various classes of substances, of which the aromatic and unsatd. hydrocarbons are more difficultly handled than the acids, bases and phenols. For the detn. of the aromatic and cyclic unsatd. hydrocarbons, the liquid-SO₂ method cannot be used, nor fractionation, nor the formolite method. The only remaining procedure is to det. the aromatic and unsatd. hydrocarbons on oil fractions free from acids, bases and phenols, by Me₂SO₄, and the unsatd. hydrocarbons by the Hg(OAc)₂ method of Engler and Tausch. Seppis, by the last 2 methods were carried out on gas benzine, benzine from wash oil, tar benzine, and tar, and the results are recorded and discussed. The tar fractions show an increase in the % of aromatic hydrocarbons with increase in the b. p., from 9.5% aromatics in the 150-200° fraction up to 26% in the 300-50° fraction. Above 250° the % of unsatd. hydrocarbons decreases.

C. B. EDWARDS

Organic extraction and absorption medium (SCHMITT) 13. Mist explosions (HABER, WOLFF) 24.

LITINSKY, L.: *Wärmewirtschaftsfragen*. Leipzig: Otto Spamer. 194 pp. 3s.-9d., bound 4s. 2d.

Mineral Industry of the British Empire and Foreign Countries. Coal and Coke and By-Products, 1919-21. Imperial Mineral Resources Bureau. London: H. M. Stationery Office. 135 pp. 4s. 6d.

Report of the Fuel Research Board for the Years 1922-1923. 1st Section: The Production of Air Dried Peat. Issued by Dept. of Scientific and Industrial Research. 146 pp. 5s. 4d. post-free. Reviewed in *Chem. News* 127, 46(1923).

SINNATT, F. S., et al.: Coal and Allied Subjects. Bulletins 1 to 10 of the Lancashire and Cheshire Coal Research Association, 1918 to 1921 inclusive. London: H. F. & G. Witherby. 205 pp. 15s. net. Reviewed in *Ind. Eng. Chem.* 15, 984(1923).

Fuel. H. CURTIES. *Brit.* 193,148, Nov. 18, 1921. A fuel for use in firing bricks, etc., is prepd. from Norfolk and other oil shales by grinding the shales to powder and mixing therewith KNO₃ in varying quantities according to the compn. of the shale.

Fuel. E. F. LOEFGREN. *Swed.* 52,141, July 12, 1922. Charcoal or peat is spread out in a layer of suitable thickness and wood tar is poured over under const. stirring. Wood-spirit (the mixt. of methanol, acetone, AcOH, etc., obtained by wood distn.) eventually with addn. of turpentine or petroleum, may also be poured over the materials before the addn. of the tar. The mass is then covered with sawdust, pulverized charcoal or peat-dust to absorb the fluids and prevent the clogging together of the mass, which is finally dried.

Burning limestone, etc., with poor fuels. S. V. BERGH. *Swed.* 51,341, Mar. 29, 1922. Bituminous alum-slate or other fuels high in ash are submitted to destructive distn. in a retort. The red-hot residues are fed under the kiln directly from the retort by means of an automatic app. especially fitted for burning such fuels. The distn. products are used in ordinary ways.

Carbonizing wood, peat, etc. G. G. FUNQVIST. *Swed.* 54,426, May 2, 1923. The carbonization is effected by means of hot, circulating gases. From the heating app. these are divided into one or more currents which are conducted severally to their resp. distn. chambers, one or more of which serve as carbonizing chambers and the others as drying and preheating chambers for the volatilization of water and turpentine oils. The gases are severally treated for separating the distn. products and again passed through the heating app.

Utilizing peat, wood waste, etc. F. W. BRANDES. *Swed.* 53,129, Dec. 6, 1922.

The combustion products from a regenerator, recuperator or another heating app. are used to heat externally two or more producers or retorts through which the raw materials are made to pass. The gases formed by the destructive distn. are freed from NH_3 and org. tar compds. and after a subsequent heating are again applied to the producers or retorts at the ends of discharge.

Improving peat and other poor fuels. F. W. BRANDERS. Swed. 53,128, Dec. 6, 1922. The gases from the destructive distn. of peat or other fuels are passed through another poor fuel, such as bog-moss and wood waste, in a special app. at a suitable temp. and without additional application of steam. The latter materials are somewhat dried by the heat and impregnated by the condensed tar. The gases are cooled and cleared for the use in burners or engines.

Utilizing bituminous alum-slate and other poor, bituminous fuels. S. V. BIRCH and K. E. LARSSON. Swed. 52,861, Dec. 13, 1922. The slate is subjected to destructive distn. in horizontal or inclined retorts under application of steam or inert gases. The gases and gaseous products obtained are utilized in the usual ways. The retorts are provided with mech. arrangements for the automatic, continuous advancing of the materials during the distn. They are mounted above a chain-roaster or another app. for the continuous advancing and burning of the coked materials which are in the red-hot state directly fed and burned under the retorts, eventually with addn. of richer fuels. The main object of this procedure is to obtain a high output of oil and a certain quantity of combustible gas. The distn. should be carried out mainly by the heat produced by the burning of the slate-coke.

Destructive distillation of poor fuels. AKTIEBOLAGET SVENSKA SKIFFERVERKEN. Swed. 52,686, Sept. 13, 1922. The distn. is carried out in a furnace which is charged alternately with red-hot, incompletely carbonized materials and cold, fresh materials.

Cutting machine for peat. K. H. V. v. PORAT. Swed. 51,297, Mar. 29, 1922.

Treating coal. W. W. STENNING, P. T. WILLIAMS, W. H. BEASLEY and A. B. MIDDLETON. Brit. 193,466, Nov. 18, 1921. In a process for treating finely divided coal, such as is described in 155,875, the coal particles are agitated in a circuit liquor with finer particles which have been previously coated with a flocculating medium which may be of the kind, such as anthracene oil or tar, producing flocculation in the cold, with or without further addn. of flocculating medium. Preferably the finer particles are coated by agitation in aq. suspension with the medium. On one example coal duff is coned. by froth flotation and the pulp is screened, the finer particles mixed with H_2O being agitated in froth-flotation app. with anthracene oil to the amt. of, e. g., 1% on the total wt. of coal. To a circuit liquor at 80° are added the coarser particles and the flocculated finer particles together with 4% of molten or finely divided solid pitch, the mixt. being agitated preferably with aeration. The solid material separable from liquor by decantation, screening, etc., is briquetted. Another coal consisting of bright and dull coal with carbonaceous shale is coned. by froth-flotation and the finer portion is flocculated in a hot acidified circuit liquor with a binding medium of pitch with tar or naphthalene. The coarser particles are then added during agitation, and the whole material after flocculation is drained, briquetted and coked at a temp. rising to 1040° . Cf. 151,236.

Gas mantles. F. HILLER. Brit. 193,259, Feb. 7, 1922. A method of fastening inverted incandescent gas mantles to their holders consists in coating the groove of the holder with small amts. of alkali phosphates, which are easily fusible in their water of crystn., mounting the mantle on the holder, preferably by means of a combustible textile or paper thread, and burning off.

22—PETROLEUM, LUBRICANTS, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

Research for the petroleum industry. R. F. BACON. *Ind. Eng. Chem.* 15, 888-90 (1923).—Brief discussion of some conventional and some speculative problems.

W. F. FARAGHER

Petroleum—A short story. J. N. TAYLOR. *Am. J. Pharm.* 95, 292-8 (1923).—A discussion of petroleum and its products.

W. G. GAESSLER

Lubricating oils from lignite tar. J. MARCUSON and F. BÖTTGER. *Mitt. Materialprüfungsamt* 40, 250-2 (1922).—A lubricating oil (I) from low-temp. tar and one (II) made by condensing with ZnCl_2 the non-viscous oils from high-temp. distn. of liquids

were investigated. The phys. consts. of (I) were as follows: d_4^{20} 0.970, flash point (open cup) 171°, Engler degrees at 20° 24.1 and at 50° 3.92. The consts. for (II) were: d_4^{20} 0.976, flash point (open cup) 198°, Engler degrees at 20° 34.9 and at 50° 5.46. Asphaltic constituents were sepd. by means of normal benzine (6.2% for (I) and 4.4% for (II)). From the benzine soln., N bases were extd. with a soln. of HCl (0.3% for (I) and 0.2% for (II)). The benzine soln. was then washed free from acids and phenols with 10% soln. of NaOH (4.2% for (I) and 1.0% for (II)). Other data obtained were as follows for (I) and (II), resp.: acid no., 1.6 and 1.9; sapon. no., 11.5 and 6.0; I no. (method not specified), 45.0 and 34.0; and S content, 1.4 and 2.7%. The acetyl nos. found were: before hydrating (method of Grün and Ulbrich), 26 and 17; after hydrating 35 and 27. The presence of ketones in considerable quantities is indicated by these values. The approx. % of S compds. are 5 times the % of S present in each oil. The formolite nos., 57 and 60, indicate the presence of 46 and 48% cyclic unsatd. compds., resp. Part of these compds. contain S, as was shown by the change in the S content following the formolite test. The presence of ketones is considered characteristic for lignite tar lubricants since only a steam cylinder oil was found to contain a small % of phenols. Naphthenes, polynaphthenes, paraffins and olefins also were present in each oil.

W. F. FARAGHER

Factors controlling behavior of asphalt mixtures. J. C. MORRELL AND LESTER KIRSCHBRAUN. *Chem. Met. Eng.* 29, 362-4 (1923).—Mixts. of steam-refined and air-blown asphalts have been investigated. Penetration and elongation curves show max. values, higher than those of either constituent. M. p. curves show a min. value, slightly lower than the m. p. of the asphalt melting at the lower temp. These values are discussed from the point of view of the phase rule, "eutectics" and the possible formation of solid solns. Mixts. of a 20° B ϕ fuel oil (28° Saybolt Furol at 77° F.) and a cracked residuum made from it (99° Saybolt Universal at 100° F.), were made, and the viscosities and cold-tests detd. The curves of viscosity have the usual form. The cold-test curve has the general form of the m. p. curve of the mixts. of asphalts. The benefit of the low cold-test of cracking still residuum in mixts. is emphasized.

W. F. FARAGHER

Notes on the quantity and properties of charcoal obtained from various kinds of Siamese woods. G. BOSSONT. *Chem. News* 127, 114-6 (1923).—Charcoals from several species were examd. as to their suitability for use in explosives. *Pithecolobium dulce* and *Serbania grandiflora* gave the best yields; *Erythrina indica* and *Alstonia scholaris* gave the most rapidly burning charcoals.

E. H.

Organic extraction and absorption medium (SCHMIDT) 13. How was petroleum formed? (BJERREGAARD) 8. Pulverizing paraffin, etc. (Swed. pat. 50,694) 13. Separating liquids by distillation (Brit. pat. 193,030) 13.

DAVIN, E.: **Le Mazout.** Paris X ϵ : A. D. Cillard, 49 rue des Vinsigriers. F. 20. Packing & Postage F. 1.50 (France) F. 2 (foreign) extra.

HAWLEY, I. F.: **Wood Distillation.** American Chemical Society Monograph Series. New York: Chemical Catalog Co. 136 pp. \$3 net. Reviewed in *J. Franklin Inst.* 196, 278 (1923); also *Ind. Eng. Chem.* 15, 981 (1923).

Cracking hydrocarbons. GULF REFINING CO. Brit. 193,188, Dec. 7, 1921. In cracking petroleum oils to produce gasoline, etc., by heating with $AlCl_3$, fresh $AlCl_3$ is added to the still in the form of a magma prepd. by mixing the chloride with a portion of the high-boiling oil at a temp. of about 150° F. The stills are formed with stirring devices carrying chains which drag over the base. When pitchy matter contg. the exhausted chloride settles to the base, it may be withdrawn without interrupting the operation of the stirrers. A suitable construction is specified.

Refining hydrocarbons. PLAUSON'S (Parent Co.), LTD. Brit. 193,521, Nov. 29, 1921. Gaseous, liquid, and solid hydrocarbons are purified, and satd. and unsatd. hydrocarbons are sepd., by agitation with a chlorohydrin or other chlorinated alc., preferably in presence of air or other gas, and preferably at 40° to 60°. In an example, 100 parts benzene are vigorously shaken with 5 parts α,α -dichlorohydrin, preferably in an emulsifier or in the colloid mill described in 155,836 (C. A. 15, 1788), and allowed to stand for 5 to 10 min.; the upper layer of purified benzene is withdrawn, and the lower layer is fractionally distd. to recover the chlorohydrin from the unsatd. hydrocarbons and other impurities. 100 parts of petroleum or crude petroleum jelly are similarly treated with 5 to 10 parts of α,β -dichlorohydrin or a dichlorohydrin mixt., resp. Cf. C. A. 16, 1861-2.

Cracking and purifying hydrocarbon oils. PLAUSONS (Parent Co.), LTD. Brit. 193,071, Aug. 16, 1921. High-boiling hydrocarbon oils are transformed into lower-boiling oils and freed from S by distg. in presence of, or by passing the vapors over, a mixt. of CaO and a Zn compd. which will react with H_2O , e. g., $ZnCl_2$. $MgCl_2$, such as sand, glass, porcelain or coke, may be added. A suitable construction is specified.

Purifying oils. A. RIALLAND (née PERCEVAULT). Brit. 193,029, Jan. 31, 1923. Mineral oils, before or after use, are freed of tar and other impurities by stirring with H_2O , and then with H_2SO_4 of 66° Bé. mixed or not with fuming H_2SO_4 , centrifuging the decanted oil or the mixt., washing with alkalies, and centrifuging or otherwise removing the H_2O , etc.

Distilling shale, etc. J. PINTSCH AKT.-GES. Brit. 193,276, Feb. 23, 1922. In distg. shale or liké bituminous fuels by internal heating with hot gas obtained by the gasifying of the shale residues with air or steam or a mixt. of these, the amt. and temp. of the gaseous distg. medium is regulated between the gasifying and the distg. chambers by the introduction of cold gas or air.

Lubricants. VILLIERS LONDON CO. AND E. R. OTTO. Brit. 193,699, Oct. 19, 1921. Castor oil, for use as a lubricant is heated with a small proportion, say up to 5%, of a metallic salt of stearic or other higher fatty acid, the alkali salts being preferred. The process may be effected by heating castor oil with caustic alkali or other base. Heating is continued to a temp. exceeding that at which the oil appears to boil. The viscosity of the oil is increased, and its liability to carbonize is reduced.

Acetic acid from charcoal furnace gases. AKTIEBOLAGET MARKS KOLUGN. Swed. 53,382, Jan. 10, 1923. After the sepn. of the tar the gases are passed through a drying system consisting of (1) a no. of smaller towers provided with arrangements for injecting milk of lime and each tower fitted with a special collecting tank outside the tower for removing mud during the working, and (2) a larger tower in which the gases are cleared and freed from lime particles carried along by the draught.

23—CELLULOSE AND PAPER

CARLETON E. CURRAN

The composition of esparto cellulose. E. L. HIRST. *Rept. Brit. Assoc. Advancement. Sci.* 1922, 358.—*Acetylation of esparto cellulose* by a modification of Barnett's method gave almost quant. yields of acetates without loss of the pentose residue. The acetate mixt. completely dissolved in acid MeOH in sealed tubes at 130°, yielding Me-glucoside and Me-pentoside. The pentose was identified as xylose, which was confirmed by isolation from esparto cellulose of a pentosan which on hydrolysis was converted to a reducing sugar identical with xylose. Assuming that no other hexose or pentose is present in esparto cellulose, the yield of Me-glucoside was 95%, and Me-xyloside 68.5%. The loss is due to decompn. of pentose to furfural. The results indicate that esparto cellulose is at least 90% a definite compd. composed of glucose residues and xylose residues in the proportions of 80% and 20% resp. C. C. DAVIS

Studies on cellulose. III. Viscosity determination of cellulose (solutions). M. NAKANO. *J. Chem. Ind. Japan* 25, 899-910(1922); cf. *C. A.* 16, 2987.—Special precautions which must be taken in the prepn. of cuprammonium solns. are given. The viscosity of cuprammonium solns. of cellulose decreases with time until it attains a const. value. A dil. soln. attains a const. value more quickly than a concd. one; the viscosity of a very dil. soln. is const. from the beginning. With solns. of the same concn., the lower the viscosity the less is the difference between the final and the initial values. The viscosity increases much more quickly than the concn. The relative viscosity increases with the temp. No appreciable decrease of viscosity due to loss of NH_3 can be observed. O and light have the greatest effect on the viscosity. The NH_3 complex of Cu has a strong oxidase-like action on cellulose. Depolymerization of the mol. aggregate of cellulose is due to the light. Of various previous treatments to which the cellulose was subjected, the most important in its effect on the viscosity was thermal treatment. J. S. C. I.

A new direct solvent for cellulose: calcium thiocyanate. ANDRÉ DUBOSC. *Rev. prod. chim.* 26, 507-10(1923).—D. claims priority for the discovery of the solvent power of thiocyanates towards cellulose and reviews Williams' results (*C. A.* 16, 340).

Ammoniacal copper oxide as a reagent for cellulose. O. DISCHENDORFER. *Z. Mikroskopie* 39, 97-121(1922); *Chimie et industrie* 10, 129(1923).—To prep. as pure a cellulose solvent as possible, prep. well washed cryst. $Cu(OH)_2$ (according to Böttger,

or other gases is overheated and applied to the liquid in the distn. app. to which it gives off its excess of heat. That part of the distn. vapors that does not take part in the circle process is taken out, eventually under pressure, and the heat utilized for other purposes, while the content of org. acids is recovered by conducting the vapor through milk of lime.

Utilizing the heat of the liquor tapped off from sulfite boilers. E. FROM. Swed. 52,976, Nov. 15, 1922. The used liquor is conducted through one or more heat-exchanging app. through which the fresh sulfite liquor is also passed in counter-current, the liquor circulating in a closed system.

Recovering sulfur dioxide from cellulose liquor. H. A. E. NILSSON. Swed. 51,399, Apr. 5, 1922. The liquor is driven from the boilers into a closed vessel by means of the pressure in the boilers. SO_2 and some H_2O are disengaged and drawn off into an acid-container by suction induced by keeping the liquid in this container in continuous circulation through an ejector connected with the container. The suction force of the ejector is regulated so as to maintain a pressure in the container approx. corresponding to atm. pressure.

Sugar from sulfite waste liquor. P. G. EKSTROM. Swed. 51,682, May 10, 1922. Waste liquor or other liquids low in sugar are enriched with this compd. by addn. of starch-contg. products such as wastes from bakeries, which products are treated at increased temp. with a dil. acid, e. g., the SO_2 in the waste liquor. The resulting liquid is worked for sugar or fermented to alc.

Pressing arrangement for cellulose-drying apparatus. F. A. B. BESKOW and A. W. NILSSON. Swed. 51,448, May 10, 1922.

Arrangement of cellulose machines for regulating the water content of the pulp layer. T. A. P. HUMBLA. Swed. 52,720, Sept. 13, 1922.

Rotary press for removing water from fibrous materials. AKTIEBOLAGET KARLSTAD MEKANISKA VERKSTAD. Swed. 52,722, Sept. 13, 1922. Mech. features.

Removing water from fibrous liquids by pressing-rollers. AKTIEBOLAGET KARLSTADS MEKANISKA VERKSTAD. Swed. 52,787, Sept. 27, 1922. Blast, preferably hot, is applied to the mass between the rollers at the places of highest pressure.

Rollers for pressing out water from wood- or paper-pulp. C. G. HOEGMAN. Swed. 52,618, Aug. 23, 1922. Mech. features.

Filter cylinder for wood pulp. AKTIEBOLAGET KARLSTAD MEK. VERKSTAD. Swed. 50,529, Jan. 4, 1922. A rotary cylinder encircled by filter cloth is divided into several chambers. The pulp is applied on that part of the rising side of the cylinder surface which is situated above the horizontal plane through the axis. A suction room is arranged inside of the chambers in such a way that a certain filter chamber is not connected with the suction room before the pulp layer is formed on the surface of this chamber.

Apparatus for taking up wood pulp. AKTIEBOLAGET KARLSTAD MEK. VERKSTAD. Swed. 50,530, Jan. 4, 1922. Structural features regarding a roller pressing against the filter cylinder. Cf. preceding abstr.

Centrifugal sorting apparatus for wood pulp. B. KIHLGREN. Swed. 52,126, July 5, 1922.

Counteracting the formation of scale in evaporating apparatus for sulfite waste liquor, etc. H. O. V. BERGSTROM. Swed. 53,794, Feb. 14, 1923. The scale is subjected to the action of liquids which transform the neutral sulfites into sol. acid sulfites, for instance aq. SO_2 or fresh sulfite liquor.

24—EXPLOSIVES AND EXPLOSIONS

C. E. MUNROE

Explosives and explosions. HENRY LEFFMANN. *Am. J. Pharm.* 95, 350-6 (1923).—Historical review.

Safety explosives and gallery tests. E. LEMAIRE. *Ann. mines Belgique* 23, 649-97 (1922); *Chimie et industrie* 10, 110 (1923).—Polemical against Audibert (C. A. 16, 2606).—L. outlines wherein the problem of safety explosives consists. A. P.-C.

War-time manufacture of tetryl. W. LEE TANNER. *Chem. Met. Eng.* 29, 404 (1923).—A concise description of methods employed in the manuf. of tetryl to meet Brit. specifications, the rapid tests for purity and stability that were developed, and the means employed for recovering spent acids and nitrous fumes. C. E. MUNROE

What the U. S. Bureau of Chemistry is doing to prevent industrial plant dust explosions and fires. D. J. PRICE and L. J. TROSTEL. U. S. Dept. of Agr. reprint from *Hartford Agent* for Apr., May and June, 1923. Pamphlet. 11 pp. C. E. MUNROE

Composition of pyrotechnic mixture for whistles. DOMENICO LODATI. *Giorn. chim. ind. applicata* 5, 234(1923).—A mixt. of 87 parts K picrate and 15 KNO₃ answers the purpose of the com. mixt. used in pyrotechnic whistles. ROBERT S. POSMONTIER.

Mist explosions. F. HABER AND H. WOLFF. *Z. angew. Chem.* 36, 373-7(1923).—Explosion limits and propagation velocities of homogeneous combustible gas mixts. have been fully investigated, but not so the non-homogeneous fuel-mist and air mixts. so important in internal-combustion motors. Petroleum (180-220), tetralin and quino-line were investigated. Lab. app. is described for prepg. ordinary mists and sepg. therefrom droplets having diams. greater than $\frac{1}{100}$ mm. by gravity and centrifugal force, and allowing to pass only a mist carrying droplets less than $\frac{1}{10000}$ mm. diam. Expansion through an orifice and introduction of cold air are made use of, and temp. is held const. Propagation velocities were detd. by a Boulaugé chronograph, the "breaks" being caused by rupture of tin-foil strips. The total wt. of droplets in a given vol. was detd. by filtering through a special filter paper and weighing same. The Sven-Oden method was used to det. the size of droplets. Results show that mists of inflammable liquids and air have the same explosion limits as the same amt. of inflammable liquid in the vapor form in air, but show less complete combustion and lower propagation velocities. H. M. SYMMES

A severe benzene and tetralin explosion. OTTO MEZGER AND FRITZ EGGER. *Chem.-Ztg.* 47, 381-2(1923).—While 3 workmen were scrubbing out a buried crude oil tank with a benzene-tetralin mixt. a violent explosion of the vapors was caused by abrasion and grounding of the extension lamp cord against the sharp edge of the man-hole. Three men were killed, one by burns and two by CO poisoning. Proper precautions against toxicity of such vapors or the use of properly protected lamp cord had not been observed. References to literature on toxicity of hydrocarbon vapors are given. The owners are blamed for lack of precautions. H. M. SYMMES

Quantity and properties of charcoal obtained from various kinds of Siamese woods (Bossoni) 22. Properties of powders (Walker) 2.

25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

The work of the Color Laboratory of the Bureau of Chemistry. J. A. AMBLER. *Am. Dyestuff Rep.* 12, 615-20(1923). E. H.

The development of the fast dye industry. J. I. M. JONES. *J. Soc. Dyers Colourists* 39, 199-203(1923).—A brief history of the fast dye industry and particularly of the vat dyes. CHAS. E. MULLIN

The valuation of dyestuffs by titration methods. R. B. BROWN AND HAROLD JORDAN. *J. Soc. Dyers Colourists* 39, 203-9; *Am. Dyestuff Rep.* 12, 585-90(1923).—A short review and discussion of the various methods of dye testing are followed by a description of a volumetric method of titrating one dyestuff with another dyestuff of a different class. Best results were obtained by the addn. of the acid to the basic dyestuff soln.; the use of widely different colors, e. g., blue with red, and green or blue with yellow; and with solns. contg. about 2 g. dyestuff per l. The end point was detd. by spotting on filter paper. Some details are given for the titration of auramine soln. contg. AcOH with indigo carmine; methyl violet with naphthol yellow S; and Victoria blue B with tartrazine. Certain other basic dyes are more readily titrated and give a clearer end point with an acid dye soln. contg. 1 g. dye with 2 g. tannic acid and 2.5 g. NaAcO per l. In this way brilliant or malachite greens are titrated with orange II; magenta or safranine with indigo carmine; methylene blue with crystal scarlet; and rhodamine B or 6G with orange MNO. Acid dyestuffs are cst'd. by titrating 25 cc. of the basic dyestuff soln. with the acid dyestuff soln. For instance, Victoria blue is titrated with orange II, and malachite green with eosin. Chrysophenin or benzopurpurin 4B solns. contg. 2 g. dye and 2.5 g. Na₂CO₃ per l. are pptd. hot by an excess of Victoria blue soln., and the excess blue is titrated with orange II. In order that results on different samples of the same dyestuff may be comparative, dyestuff solns. of approx. equal strength should be used, e. g., the soln. of the weaker dyestuff should contain more dyestuff than the stronger dye soln. CHAS. E. MULLIN

Sulfur and mordant dyes. GEORGE EMMONS. *Am. Dyestuff Rep.* 12, 599-603 (1923).—Directions are given for the use of Katigene dyes and for special uses of S

dyes on silk. The procedures for dyes on silk with Al, Cr, and Fe, resp., as mordants are described.

L. W. RIGGS

Simple and practical method for determining the quality of textiles and their protective values. ARCIERO BERNINI. *Giorn. chim. ind. applicata* 5, 169-71(1923).—H. has constructed a pocket and an office type of instrument called a "lanasetoscope," essentially a gold leaf electroscope, for the measurement of the insulating power toward electricity of a textile. In this way one may det. whether a textile is of pure wool or pure silk or if instead it is composed of cotton, artificial silk or other vegetable textile fiber, or if of wool or silk, whether it is overworked or loaded. Description and photographs of the instrument are given.

ROBERT S. POSMONTIER

Hydrogen peroxide bleaching. I. E. WEBER. *J. Soc. Dyers Colourists* 39, 209-14 (1923).—One vol. H_2O_2 is almost completely decompd. in 2 hrs. by 0.1% $Fe_2(SO_4)_3$ and with 1% the decompn. is complete in 1 hr. With $CuSO_4 \cdot 5H_2O$ the decompn. is about 66% in 3 hrs. with 0.1%, and with 1% the loss is 89%. Data are given on the decompn. of acid and alk. H_2O_2 in the presence of 15 metals. Acid H_2O_2 is decompd. by Cu and its alloys, including monel metal, but Pb, Sn, Sb and Ni affect it very little. H_2O_2 neutralized to phenol red with Na silicate is little affected by metals but when NH_4OH is used to neutralize it, Cu and Pb decomp. it rapidly. When 6 vol. H_2O_2 is neutralized to methyl orange the decompn. is 9-10% on standing 8 days at 18°. When phenol red is used as indicator, the decompn. is about 30%, and with phenolphthalein about 35%. In 1 vol. H_2O_2 at 37° the decompn. in the presence of 0.1% NH_4OH is about 24% in 3 hrs., and with 1% NH_4OH about 68%. In the presence of even 1% Na silicate the decompn. is less than 1% in 3 hrs. This economy of Na silicate in bleaching has been proven on a large scale. The bleaching of wool, cotton, silk and unions is briefly discussed. The after-treatment of S dyes with H_2O_2 in alk. soln. is rapid, gives purer tones and tendering is reduced. Four curves and 2 tables. CHAS. E. MULLIN

Permanganate of soda as a bleaching agent. WM. B. NANSON. *Am. Dyestuff Rept.* 12, 556-60(1923).—Several methods for prepg. the $NaMnO_4$ are described and details are given for bleaching wool, cotton, jute, ramie and similar vegetable fibers.

L. W. RIGGS

Unshrinkable finish on wool. S. R. TROTMAN. *Am. Dyestuff Rept.* 12, 611-2 (1923).—Theories relating to shrinking and felting are discussed, also the properties of chlorinated wool. Expts. are under way for the purpose of finding a quant. basis for the treatment of wool by Cl to which scientific control may be applied.

L. W. RIGGS

Relation between the indican content of Java indigo and the kinds of nitrogenous fertilizers (JOSHI) 15. Evaporation of water from wool (FISHER) 13.

BAUER, K. H.: *Monographien aus dem Gebiete der Fett-Chemie.* Pt. III. Die Oele und Fette in der Textilindustrie by HERBIG. Stuttgart: Wissenschaftliche Verlagsgesellschaft m. b. H. 302 pp. 6s. 5d.

Dyes. A. H. DAVIES, R. F. THOMSON, J. THOMAS AND SCOTTISH DYES, LTD. Brit. 193,431, Sept. 27, 1921. *Dibenzanthrone compds., dinaphthalimides*, and other "ketonic perylenes," i. e., compds. in which the perylene nucleus has attached to it in the 3,4- and 3',4'-positions pairs of rings contg. ketonic groups, are converted into oxidation products by treatment with MnO_2 and H_2SO_4 , or other oxidizing agents, such as HNO_3 . Treatment of the oxidation products with mild reducing agents such as $NaHSO_4$ converts them into reduction products. Both the oxidation products and their reduced derivs. are vat dyes and may be converted into other vat dyes by treatment with alkylating or acylating agents. Instead of oxidizing the parent compds. and then reducing, hydroxy groups may be introduced by nitrating, reducing, diazotizing, and boiling the diazo compd. The alkylation or acylation may be effected in the presence or absence of inert solvents, such as nitrobenzene. The several products form additive compds. with H_2SO_4 which may be isolated and then decompd. by H_2O to give a purified dye. The oxidation products or their reduced derivs. may also be purified by acetylating and then hydrolyzing the acetyl compds. Parent materials are specified.

Dyes. SOC. ANON. POUR L'IND. CHIM. A. BALE. Brit. 193,385, Jan. 25, 1923. *Monazo dyes* which yield black shades on wool when after-chromed are prepd. by coupling a diazotized unsulfonated 4- or 6-nitro-2-aminophenol with 1-amino-5-hydroxynaphthalene-7-sulfonic acid in the presence of $Ca(OH)_2$. In an example 4-nitro-2-aminophenol is used as diazo component.

Textile fibers. E. LANG. Brit. 193,014, Jan. 19, 1923. In the manuf. of textile fibers from animal hair and bristles, wherein the fibers are first treated with chlorinating or oxidizing agents, the oxidized fibers are subsequently treated with a soln. of an alkali such as NaOH of such strength as to be used up in forming a salt, leaving the albuminous substances unattacked and thus avoiding loss in wt. In an example, 30 l. of a 1 to 15% soln. of alkali are used per kg.

26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

Casein colors and paints. MAURICE DE KEGHEL. *Rev. prod. chim.* **26**, 469-72, 501-6(1923).—A description of the prepn., properties and uses of water colors having a casein binder, casein paints (for art work), and casein varnishes. F. A. WERTZ

A new paint mill. G. H. LENART. *Farben-Ztg.* **28**, 1391-2(1923).—A horizontal shaft has a 30 cm. disk of steel or porcelain mounted on one end. The pressure of this disk, revolving at 1000 r. p. m. against a similar stationary disk housed in a H₂O-cooled enclosure, can be regulated. Paint or enamel of ready mixed consistency forced between the disks is ground exceedingly fine. The mill has 5 to 15 times the output of the largest roll mills. Illus. F. A. WERTZ

Colloid theory and painting. A. EHRNER. *Kolloid-Z.* **32**, 343-9(1923).—Review. Cf. C. A. **16**, 4357. F. A. WERTZ

New lakes and pigment colors. HANS WAGNER. *Farben-Ztg.* **28**, 1386-9(1923).—A descriptive summary and tabulation of the characteristics, designations, etc., of newer lakes and colors used in the printing ink and paint industries. F. A. WERTZ

Paper and printing inks. RÜBENCAMP. *Farben-Ztg.* **28**, 1389-90(1923).—Under certain circumstances, printing inks may affect the discoloration and durability of the paper to which it is applied, but such defects which develop are more often inherent in the paper itself. F. A. WERTZ

Tetralin varnishes. E. O. RASSER. *Chem.-Ztg.* **47**, 660-1(1923).—Review. F. A. WERTZ

Varnish gums. F. W. BURNSIDE. *Paint, Oil and Chem. Rev.* **76**, No. 5, 8-9 (1923).—A review of the origin and properties of the various kinds of gum used in varnish making. F. A. WERTZ

Preparation of coumarone resin. S. HIRANO. *J. Chem. Ind. Japan* **25**, 827-33 (1922).—On slowly adding 5 cc. of concd. H₂SO₄ to 100 cc. of purified coal tar naphtha, b. 155-185°, with const. stirring, coumarone resin is produced, with a yield of 9.53% of the naphtha. The naphtha should be previously washed with soda lye (sp. gr. 1.22) and dil. H₂SO₄ (sp. gr. 1.20) to remove tar acids and bases, and freed from water. If the alkali washing be omitted, the same yield is obtained, but the product is darker in color. The initial temp. of the oil should be as low as possible and rise of temp. during the reaction avoided. When more oil is used at a time, the quantity of the acid should be decreased to avoid oxidation. A paler resin is obtained by washing the reaction product with alkali. As polymerization reagents, SnCl₄ (5 cc.) gives a hard and pale resin (m. p. 85°), the yield being 6.06 g. from 100 cc. of oil, while AlCl₃ (10 g.) gives a soft and dark resin (m. p. 38°) with a yield of 32.5 g. J. S. C. I.

A fast ink for use in paper mills (VANDERSTICHEL) 23. Pulverizing resins, etc. (Swed. pat. 50,694) 13.

Shellac substitute. I. R. KOEHLER. Swed. 53,760, Feb. 14, 1923. Oxidized amorphous resin acids are mixed with cellulose esters or mixts. of such esters with camphor or camphor substitutes.

Resins and similar products. G. F. MAGNUSSEN. Swed. 54,434, May 2, 1923. Lignites, wood, etc., are extd. in a series of vessels at a temp. below the b. p. of the extrn. liquid. The soln. is distd. in a column app.

Increasing the copying power of ink. P. G. V. ROSENDAHL. Swed. 53,257, Dec. 27, 1922. By mixing the ink in liquid or solid state with glycol.

27—FATS, FATTY OILS, WAXES AND SOAPS

E. SCHERUBEL

California olive oil. W. V. CRUESS. *Chem. Met. Eng.* 29, 222-3(1923).—About 200,000 gal. of oil is produced annually from fruit unsuitable for pickling. This oil can be treated with good results by adding 2% of finely ground bone black to remove excess color and 0.2% Na_2CO_3 and 0.3% H_2O by vol. to remove free fatty acids, 1% by wt. of Filter-Cel is added before final filtration. The mixt. is heated for 2 hrs. at 190°F . and stirred with a mech. agitator. After filtration the oil is clear, light-colored and of neutral flavor and after several mos. a flavor similar to that of high-grade Italian oil is developed.

E. SCHERUBEL

Composition of stearin pitch. HUGO DUBOVITZ. *Chem.-Ztg.* 47, 616-7(1923).—The % of pitch produced is related to the I no. of the fatty acids distd., high I nos. giving a higher %. Sunflower seed oil fatty acids were heated in a stream of CO_2 with the following results:

	Original fatty acids	1 hr. at 340°	2 hrs. at 340°
I no.	137.1	104.9	87.96
Acid no.	197.5	173.0	19.42
Sapon. no.	199.5	179.7	56.48
Unsaapon.	0.50%	8.88%	87.78%
Color	yellow	brown	blackish brown
Fluidity	thin	thick	solid

By distg. off $1/2$ of the above the I no. of the distillate became 109.5 and of the residue 118.0 and upon distg. all of the above the I no. of the distillate was 109.8. A herring oil of 123.6 I no. and 2.5% unsapon. gave upon distg. the fatty acids an I no. of 49.5 and unsapon. of 3.1% and 6.8% pitch. Distn. effects both polymerization and condensation. The examn. of the pitch is difficult. The I no. of a bone grease pitch was 50, the same as that of the fatty acids. This is due to a concn. of the difficultly distillable fatty acids; and the I no. would increase if condensation did not take place. Stearin pitch may be considered a mixt. of fatty acids, neutral fat, anhydrides, hydroxy acids, condensed fatty acids and satd. and unsatd. hydrocarbons. Its properties are due to the hydrocarbons and condensation products.

E. SCHERUBEL

Edible oils and *Corylus avellana* Lin. SAVA SALVATORE. *Staz. sper. agrar. ital.* 55, 34-50(1922).—"The kernels of all varieties of *Corylus avellana* (hazelnut) always contain considerable oil that could worthily occupy in domestic economy a place next to that of olive oil." The methods of extn. used for olive oil cannot be used. Hazelnut oil is very similar to almond oil in properties. It has $d_{40} 0.9169$; "solidifies at 18° and only liquefies at 4° ." The Tortelli thermo-oleometer reading is 35-8; the Zeiss butter refractometer reading at 25° is 61; the relative I no. is 83-90; the abs. I no., 97-8; sapon. no., 187-97; the fatty acids m. $17-25^\circ$ and solidify at $15-20^\circ$. It does not sensibly color with Heydenreich and Hauchecorne's or Brullé's reagents nor give special chromatic reactions. It turns greenish on mixing with HNO_3 contg. nitrous fumes. The fatty acids are sol. at 15° in an equal vol. of alc. and remain in soln. if the quantity of solvent is increased. It contains 10.41% glycerol. Numerous analyses of kernels and of the cake after the extn. of oil are reported. Only kernels of the current season can be used for the production of edible oil. The kernels may contain 66% of oil.

ALBERT R. MERZ

Compounds of sodium carbonate with fatty acids. J. F. WEINBERG. *Chem. News* 126, 214(1923).—Fatty acids when melted readily combine with crystd. Na carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) melted in its water of crystn. The compds. formed resemble NaHCO_3 and are represented by the formula, $\text{Na}_2\text{H}_2(\text{CO}_3)(\text{C}_n\text{H}_{2n-1}\text{O}_2)_x \cdot x\text{H}_2\text{O}$. These compds. can be used instead of soap, the effect on the skin being much milder than that of soap owing to the absence of caustic alkali. The org. N compds. exuded from the human skin, which are insol. in NaOH and in soap, are readily sol. in hot aq. solns. of these compds., so that the latter would be very valuable in laundry work. Fatty acids prepd. from a com. soap gave a product having much the same appearance as the original soap, and somewhat harder. The proportions of the ingredients may be $1/2$ part of Na carbonate to 1 part of fatty acids.

J. S. C. I.

Modern laundry processes. F. H. THIES. *Z. angew. Chem.* 36, 312-4(1923); 1 pt. —This paper is part of a polemic between T. and Heermann (C. A. 17, 1891), relative to the question: Is the "combination process," as in the use of "Persil," to be

recommended to the housewife, or washing with soap and soda with subsequent bleaching, and if the latter, what bleaching agents best assure minimal injury to the fiber? T. defines a "combination" washing compd. as having the general approx. compn.: total fatty acid 30, total alkali 18, Na silicate 2.5 and Na perborate 10%, in homogeneous mixt. On the basis of tensile strength curves of fiber against the no. of washings, for the 3 cases: bar soap, soap powder, and "Persil," T. shows that the combination process is not injurious to the fiber. While Heermann recommends household bleaching with Cl_2 or hypochlorite, he maintains that metal oxides catalyze the action of Cl_2 on the fibers analogous to corrosion by O. T. holds that chlorination always results in injury under all circumstances, and that no satisfactory antichlor is available which may be safely used even by the educated housewife. He recommends O_3 or Na_2O_3 for bleaching, as being without harmful after-effect.

THEO. F. BUEHLER

Catalytic reduction and hydrogenation (ANDERSON) 10.

Cleansing preparations. J. W. AMNER and M. E. HARRIS. Brit. 193,526, Nov. 30, 1921. A cream or paste for cleaning the hands, etc., and capable of use with or without added H_2O , is composed, in the preferred form, of 15% of oleic acid, 3% of glycerol, 5% of petroleum spirit, 3% of KOH, 30% of ground SiO_2 , and 42% of H_2O .

Purifying "sulfate-soap." E. G. PETERSON. Swed. 52,058, June 28, 1922. The odors and coloring substances in the soap obtained as a by-product of sulfate-cellulose manuf. are destroyed or transformed by treating the soap, after a preliminary cleansing, with Cl_2 or a bleaching Cl compd.

Mill for fatty seeds. N. O. LINGREN. Swed. 50,834, Jan. 17, 1922 and 50,895, Feb. 8, 1922. Structural features.

28—SUGAR, STARCH AND GUMS

F. W. ZERRAN

Filter cloths. JAR. DEDEK. Z. Zuckerind. czechoslovak. Rep. 47, 346 7(1923); cf. C. A. 16, 130-1.—D. tried to develop a new cloth which should be merely a carrier for ppt. and thus the first layers of ppt. would be the real filtering medium. One press was dressed half with this cloth and half with usual style cloths. The new cloth ran cloudy for only a very short time and its filtering rate did not fall off so that it soon was surpassing the old cloths. Cake could be washed down to about half the sugar content of cake on old cloths.

W. L. BADGER

Production of starch on a small commercial scale from root crops and corn (and the feeding value of the residue). F. G. KRAUSS. Hawaii Agr. Expt. Sta., Rept. 1921, 55-7.—Com. amts. of starch were produced from edible canna, sweet potatoes, taro and 2 varieties of cassava, with an approx. yield of 20%; the expts. with corn proved a failure. The residues, contg. approx. 50% of the total original starch, made into raw and cooked rations for swine and poultry, showed a feeding value, in the case of sweet potatoes and cassava, fully equal to corn, on a dry wt. basis, provided the proportion did not exceed 50% of the total ration. The products from edible cannas and Irish potatoes proved less palatable. The results showed that efficient utilization of the by-products could be made to cover the cost of manuf. of the starch; with the present market for the latter the process represents a profitable undertaking on a small com. scale.

P. R. DAWSON

Galvanometric method for evaluating sugars and sugar products. ANON. Z. Zuckerind. czechoslovak. Rep. 47, 398-400(1923).—A Zn-C cell is immersed in a soln. of the sugar and the resulting e. m. f. read. This is a measure of the sol. inorg. salts present, and hence helps to evaluate the sugar. Data given in the article are of no significance because a pyrometer galvanometer was used and the results were recorded in degrees. The most impure refined sugar was easily distinguished from the best raw sugar.

W. L. BADGER

Purification process and equipment for the extraction of sugar from the scum in the manufacture of sugar. ASKAN MÜLLER. Z. Zuckerind. czechoslovak. Rep. 46, 685; Chem. Zentr. 1923, II, 37.—The liquor ordinarily used for purifying the scum dissolves large amts. of deposited non-sugar material in the form of org. Ca salts. To prevent this, the purifying liquor is first treated with CaO , $\text{Ca}(\text{OH})_2$, alk. earths and their salts, etc., or other compds. which can be again pptd. by satn. Hard H_2O is softened and ammoniacal H_2O first neutralized before treatment with lime. Such a preliminary

treatment of the purifying liquor is simple and practicable and prevents incrustation of the filter cloths.

C. C. DAVIS

Distillation of ammonia from limed and carbonated beet juice and its influence on the composition of this juice. W. KOHN. *Z. Zuckerind. czechoslovak. Rep.* 46, 431-8 (1922).—In lab. expts. limed beet juice when distd. in an app. provided with a dephlegmator yielded only 0.01 and 0.016% NH_3 when the vol. of the distillates was 6 and 14%, resp. Juice which had been both limed and carbonated yielded 0.008 and 0.012%, resp. Generally juice which had been thus distd. was lower in purity, darker in color, and higher in Ca content than that obtained according to the ordinary routine.

J. S. C. I.

Comparison of the value of various decolorizing carbons for the production of white sugar in the beet factory. E. SAILLARD. *Circ. Hebd. Syndic. Fabr. Sucre* 1756(1922); cf. C. A. 17, 1730.—In large-scale expts. in a beet sugar factory, the value of various decolorizing carbons was compared by operating upon a liquor composed of virgin sirup ($1/3$) and remelt sirup from affined after-product sugar ($2/3$), 17.2 kg. of "Carboraffin" being used to every 96 hectoliters, and the other carbons added in amts. proportionate to their cost. Under these conditions "Darco" and "Norit" showed a decolorizing power, as shown by the proportion of color removed, of about 75%, and "Carboraffin" one of 64%. All the carbons were found to eliminate from soln. about the same quantities of Ca salts and nitrogenous compds., which quantities were always much less than those taken up by animal charcoal (bone black).

J. S. C. I.

Manufacture of plantation white sugar using Bach's process. C. SAILLARD. *J. Fabr. sucre* (Jan. 13, 1923).—Evaporator sirup (resulting from juice clarified with lime in the ordinary way) is cooled to 40-5°, after which it is limed and sulfited simultaneously, the action of an excess of alkali on the reducing sugars thus being avoided, and an energetic purifying effect obtained at the same time. This operation is terminated when about 2 kg. of CaO per 1000 l. of juice has been added to the sirup, and the supply of SO_2 is cut off when neutrality to phenolphthalein but barely alk. to litmus has been reached. After reheating the sirup to 90-9°, it is sent through filter-presses; filtration proceeds readily provided sufficient lime has been added, a light-colored and brilliant sirup, capable of giving a good white sugar, being thus obtained.

J. S. C. I.

By-products of the sugar industry. W. E. CROSS. *Rev. ind. agr. Tucumán* 13, 81-128(1922).—A general discussion of methods of utilizing the bagasse, filter cake, and molasses from cane sugar.

L. E. GILSON

Yield of white crystals obtained on washing (affining) raw beet sugar with water. J. ROUBINEK. *Z. Zuckerind. czechoslovak. Rep.* 47, 365-72(1923).—Raw beet sugar of good quality was mixed with heavy sirup (66 and 34%, resp., being used), centrifuged, washed with water, and the yield of white crystals ascertained under varying conditions, the following facts being elicited: whether it be 45°, 60°, or 80°, the temp. of the sirup used exerts little influence on the yield; on the other hand, the concn. of the sirup is of importance, the best results being obtained at 72.5° Brix, as compared with 68.2° and 66.7° Brix; with 4.78, 7.19, and 9.30% of water, by weight of the raw sugar, the corresponding yields were found to be 91.47, 77.00, and 73.1%, also on the raw sugar introduced. These figures are only about 1% lower than those found by Langen (*Centr. Zuckerind.* 18, 67(1909-10)), who stated that for washing a good beet sugar, about 7-8% of water by weight on the raw sugar should suffice for the production of good white crystals, but that 10% is required in the case of an inferior product.

J. S. C. I.

Hydrogen-ion determinations. Notes on their applications to cane juice clarification. W. J. WILLIAMS AND J. A. GEBELIN. *Facts About Sugar* 17, 202(1923).—H-ion detn. is suggested as a scientific substitute for "rule-of-thumb" methods now in use to control liming. Good clarification could be carried on between p_H 8.5 and 6.8 without danger of inversion. The p_H at which max. coagulation and settling occurs is optimum; this point varies with different juices. It is recommended that this point be always detd. with H-ion indicators as the only scientific method of control. This work constitutes a mfg. expt. utilizing lab. investigations of Brewster.

T. SWANN HARDING

"Ginal" process for the purification of beet and cane sugar juices. E. SAILLARD. *Suppl. Circ. hebdom. No. 1719*(1922).—"Ginal," a prepn. contg. Na alginate (cf. Brit. pat. 173,735), was mixed with beet diffusion juice heated to 75°, at the rate of 0.2 kg. per hectoliter, and milk of lime of 22° Bé. added, while stirring, until the quantity present (as CaO) was 0.2 kg. per hectoliter. Juice thus treated was passed successively through filter-presses and mech. filters, limed to about 8 g. CaO per l., carbonated at 80°, filtered, and sulfited, after which the usual course of operations was pursued. As the result of this treatment the purity and saline ratios were about the same as those in ordinary carbonatation, as was also the amt. of nitrogenous impurities pptd. On the other hand,

the clarified juices contained more Ca salts; while a marked disadvantage was the slow passage of the juice through the presses, owing to the slimy nature of the ppt., which could be detached from the cloths only with difficulty. Analysis of the press cake gave the following figures: water 44.15, sugar 1.81, N 0.25, P₂O₅ 0.50, magnesia 0.67, free CaO 2.36, and CO₂ 19.16%. It is assumed by the promoters of the process to have a value of 56 fr. per ton as a fodder or fertilizer constituent, and when this is taken into consideration the process is claimed to show an economy of 1.19 fr. per ton of roots sliced, as compared with the ordinary carbonatation process (in which about 10 times the amt. of lime is added to the raw juice). J. S. C. I.

Use of essential oils as antiseptics in the chemical control of the sugar house. HENRI COURTONNE. *Bull. soc. ind. Rouen* 51, 32-5(1923).—The antiseptic power of oil of cinnamon towards sugar-beet juice is equal to that of HgCl₂, there being absolutely no loss in sugar content in 1 month. A. PAPINEAU-COUTURE

The pressure evaporator station of the Zdic sugar factory. LUDWIG KÖPPL. *Z. Zuckerind. czechoslovak. Rep.* 47, 395-8(1923). W. L. BADGER

Report of the Prague experiment station for the sugar industry, for the year 1921-2. ANON. *Z. Zuckerind. czechoslovak. Rep.* 47, 555-62(1923). W. L. BADGER

Hawaiian starches. J. C. RIPPERTON. *Hawaii Sta. Rep.* 1921, 38-40; *Expt. Sta. Record* 48, 310.—Samples of starches extd. at the Hāiku Substation by com. methods from some Hawaiian root crops gave the following percentages of starch: edible canna 81.2, sweet potato 84.3, and cassava 83.6. Analyses of the residues from the extn. showed, however, a very low percentage extn., indicating that improvement in methods would be necessary before com. extn. could be done with profit. As a possible com. source of starch the tree fern is suggested. The core of the av. sized fern is said to weigh from 50 to 70 lbs. and to be nearly pure starch. Two samples of starch prepd. from the tree fern by the usual methods gave starch percentages of 82.01 and 83.43 as compared with 87.1 for corn starch and 82.8 for arrowroot starch. H. G.

Six types of C (SAUER) 18. Sugar from sulfite waste liquor (Swed. pat. 51,682) 23.

29—LEATHER AND GLUE

ALLEN ROGERS

Determination of insoluble material in tan liquors. CHAMBAUD, HUGONIN AND BRUN. *Cuir* 12, 325-7(1923).—The official method for detg. insol. matter gives results which do not represent the material of no tanning value. The amt. of material which can be removed by filtration varies with the diln. The filter paper is converted into an ultra-filter by contact with tan liquor, and hence much colloidal matter having tanning properties is filtered out. The detn. of insol. matter by centrifuging is recommended. Also in *J. Soc. Leather Trade Chemists* 7, 331-6(1923). H. B. MERRILL

Leather standards. A. HARVEY. *Leather World* 25, 563-4(1923).—Enumeration of difficulties involved in prep. specifications suitable for all leathers. J. A. W.

Variation in the measurement of leather due to the moisture in the atmosphere. ANON. *J. Soc. Leather Trades Chem.* 7, 309-12(1923).—Leather shrinks when the air is dry and expands when the air is wet. This, however, is to a certain extent controlled by the tanning and dressing. The discrepancies in com. measurements of leather are attributed to the fact that in 2 or 3 hrs. leather accommodates itself in size to suit the humidity. (This latter statement however is not found to be true in our experience. ABTRACTOR.) ERWIN J. KERN

Effect of perspiration on chrome upper leathers. D. WOODROFFE AND R. E. GREIN. *J. Soc. Leather Trades Chem.* 7, 305-9(1923).—A pair of boots of semi-chrome leather which cracked, upon analysis did not show an excess of either acid or alkali. They were subjected to a wear test which indicated that the perspiration introduced Na salts in the leather thereby producing brittleness. It is thought that the fabric side lining is not sufficiently resistant to the penetration of the alk. salts, and it is suggested that a good leather lining be used instead. ERWIN J. KERN

The hydrolysis of collagen by trypsin. F. L. SEYMOUR-JONES. *J. Soc. Leather Trades Chem.* 7, 293-304(1923).—Reprinted from the work by A. W. Thomas and F. L. Seymour-Jones (cf. *C. A.* 17, 2519). ERWIN J. KERN

Physical theory of tanning in the light of the Nägeli micellar theory. W. MOELLER. *Z. Leder- u. Gerb.-Chem.* 2, 45-90(1922).—A brief review is given of Nägeli's micellar theory and its bearing on the formation of leather. Liming of hide with alkalis and

swelling with acids result in a partial breaking up of the micels, and a small amt. of hide substance is found in the solns. More hide substance is dissolved by more dil. solns. of acids or alkalis. A definite amt. of hide substance is given up by the pelt to water, this amt. being const. if the hide is sterilized. All tanning agents have the common property of checking and preventing hydrolytic and fermentative decompn. of the hide for an unlimited time. 1.5% of the dry hide substance apparently lost in vegetable tanning is not really lost, because it could never take part in the tanning. Synthetic tannins do not behave like other tanning agents but like mineral acids, which hydrolyze the hide substance in proportion to the time and concn. Free H ions dissociated from free acids have a gradual destructive effect on hide substance even when it is converted into leather. All ionic theories of tanning are therefore wrong, since the result of such dissoc. is always the destruction instead of the conservation of the hide substance. Leather is hide or skin, the elements of which are protected from fermentative and hydrolytic influences. When gelatin is tanned with different mineral and vegetable tanning agents only 80-90% is tanned; the rest is in soln. in a hydrolyzed condition. Leathers tanned with synthetic tans are not very resistant to hot water, losing 50% of their hide substance, and they should be classified separately. The faults of iron-tanned leather are attributable to the dissoc. of the iron compds. in the leather. References are made to M.'s peptization theory (*C. A.* 12, 2708; 15, 190 and *Collegium* 1920, 69-79). The essential constituent of a tanning soln. is an absolutely insol. substance or a substance which forms an insol. product in contact with the hide substance. This substance must be converted into a colloid sol by peptization. Leather is produced by the adsorption and deposition of the insol. peptized substances on the individual micells of the micellar bands. J. S. C. I.

The tanning industry in Brazil. F. G. A. ENNA. *Leather World* 25, 560-2(1923).—The exasperatingly slow development of the industry in Brazil is due to lack of intelligent supervision and experienced labor. Much of the best raw stock is exported only to be returned later as finished leather. There are great latent possibilities for enterprising tanners in the abundance and variety of raw tanning materials to be found in Brazil. J. A. WILSON

The German tanning industry. GEO. J. RANDALL. *Leather World* 25, 558-60 (1923).—Great mech. improvements and rigid control systems are being instituted by German tanners at the present time which are certain to make them very dangerous trade rivals in the future. British tanners are urged to heed this warning and to study the possibilities for scientific advancement of their own tanneries. J. A. WILSON

Tanning properties of green and violet solutions of chromium salts. R. E. LIBS-EGANG. *Z. Leder- u. Gerb.-Chem.* 2, 90-6(1922).—Green solns. diffuse less quickly in gelatin than violet solns. in the first 24 hrs., but the difference is less after several weeks. A basic chrome alum soln. diffused less than either of the others. Ten % solns. of gelatin, when treated with solns. of Cr salts, required longer to set when green solns. were used than when violet solns. were used. After setting the jelly was covered with a soln. of Ba(NO₃)₂. There was no difference in the diffusion as shown by the formation of BaSO₄. Half the H₂SO₄ in the green soln. of Cr salt was not ionized, but there was no difference in the jellies, so that the H₂SO₄ in the jelly is ionized to the same extent in each. Part of the acid becomes masked by heating the jellies to 90°. Green chrome alum solns. had a greater swelling effect and less tanning effect on bone glue powder than violet chrome alum solns. J. S. C. I.

ZIEGLER, CH.: *Étude sur la tannerie et les industries connexes au Maroc.* Paris: Edited by "La Chaussure Française," 141 Boulevard Sébastopol. 123 pp. F.7.50. Reviewed in *Chem. News* 127, 96(1923).

Waterproof leather. C. G. J. AASTROEM. *Swed.* 53,398, Jan. 10, 1923. The leather is impregnated at first on the fleshy side and then on the hairy side at room temp. in a fulling mill.

30—RUBBER AND ALLIED SUBSTANCES

JOHN B. TUTTLE

Artificial rubber latexes. CAMILLO PELIZZOLA. *Giorn. chim. ind. applicata* 5, 76-7(1923); cf. *Rubber Age* 13, 190-1.—Successful attempts to prep. emulsions of rubber in Li₂O ("artificial latex") are described (cf. *C. A.* 17, 1910, 1350). This was ac-

completed in principle by prepg. a rubber soln. contg. H_2O as the disperse phase and inverting such a system to a dispersion of the rubber soln. in H_2O . The phenomena were studied by coloring the H_2O phase with an indicator (*e. g.*, phenolphthalein), by aid of the method of Robertson (*cf. Kolloid-Ztg.* 17, 7(1910)) and microscopically. Rubber solns. were thus emulsified in H_2O and constituted the disperse phase when a H_2O -sol. emulsifying agent was added. All agents which emulsify C_6H_6 and H_2O were effective. Washing soap gave the best results, starting with 1:9 solns. of rubber in C_6H_6 or benzene and adding an equal vol. of 2% aq. soap soln. On agitation, the 2 liquids formed a milky liquid consisting of minute drops of rubber soln. dispersed in the soap soln. After a time (varying within wide limits), the emulsion sepd. into 2 layers, a lower layer of excess soap soln. (contg. droplets of rubber of 1–2 μ diam.) and an upper layer of viscous cream constituting the true rubber emulsion. This cream contd. globules of varying size, the majority 5–7 μ , others 3–4 times as large and a few 1 μ . By some method more effective than simple shaking, much smaller globules should be obtained. In a system of spheres of uniform size in contact, the vol. of the spheres can be calcd. to be 74% of the total mass. In conformity with this, it was found that from emulsions of the most varied initial compn., creamy layers sepd. in which the % vol. of the disperse phase (rubber soln.) approached 74, varying from 60 to 80. The rate of sepn. was a function of the difference in d. of the 2 phases, of the viscosity of the continuous phase, and of the degree of dispersion. From rubber solns. of the same d. as the soap soln., stable emulsions could be prepd. with varying percentages of the disperse phase. Emulsions of C_6H_6 solns. of rubber in H_2O also underwent an inversion of type and were transformed into emulsions of H_2O in rubber when treated with aq. Ca, Mg or Fe salts. When a $CaCl_2$ soln. came in contact with the emulsion, the globules of rubber soln. united to form progressively larger drops, finally forming a network with H_2O as the disperse phase. This phenomenon is analogous to the coagulation of natural latex, and furthermore the degree of diln. and the concn. of the coagulant influenced the inversion of type as it does in the coagulation of latex. Rubber was pptd. from its artificial emulsions either by acids or by treatment with a liquid in which H_2O and C_6H_6 are each sol., such as EtOH. Rubber recovered from such emulsions showed the same vulcanizing properties that it had previous to emulsification. A bibliography is included.

C. C. Davis

Action of $SeOCl_2$ on pure rubber (PICK) 10.

Rubber composition. N. D. NIELSEN. U. S. 1,463,905, Aug. 7. Fish scales are combined with vulcanized rubber in order to form a tough compn. for tires, shoe parts or other articles.

Rubber compositions. ELEKTRIZITÄTSWERK LONZA Brit. 192,080, Jan. 17, 1923. Solid products obtained by condensing acetylene with finely divided metals such as Cu, their salts or alloys, or by submitting acetylene to dark elec. discharge and known as "cuprene," are employed as an ingredient in rubber, etc., compns.

Rubber compositions. E. HOPKINSON. Brit. 193,044, Feb. 7, 1923. Compound-ing materials such as vulcanizing ingredients, oils, fillers, etc., are mixed with latex to which has been added an agent to prevent premature coagulation, and the mixt. is agitated during coagulation, to secure homogeneity. Ingredients capable of absorbing H_2O from the latex may be wetted prior to mixing. Example, 2 parts of glue are added to latex contg. 100 parts of rubber to retard coagulation, and with this is mixed 10 parts of ZnO , 8 parts of S, and 200 parts of clay previously wetted if desired. The mixt. is placed in a mixing machine and agitated during drying, until the mass is in a granular state. Drying is completed in the open and the mixing is vulcanized at 60 lbs. steam pressure in an hr. Cf. 157,978 (C. A. 15, 2019).

Rubber and artificial resin compositions. FLAUSON'S (Parent Co.), LTD. Brit. 193,524, Nov. 30, 1921. Solid or liquid compns. contg. rubber and artificial resins, such as the condensation products of $HCHO$ with phenol, acetone, or furfural, are obtained by homogenizing the substances in the presence of a liquid which exerts a solvent or a swelling action upon both ingredients. The preferred liquids are chlorohydrin, cyclohexanol, and a mixt. of these. The homogenization may be effected in mills of the usual type or in a colloid mill as described in 176,003. Other solvents, fillers, or S may be added to the mixt., and the product may be vulcanized. To obtain a varnish, 20 parts of a phenol-aldehyde resin and 5 parts of rubber are allowed to swell in 50 parts of dichlorohydrin or cyclohexanol, and the mixt. is treated in a colloid mill. Alternatively the rubber may be dissolved by warming in a mixt. of these 2 solvents and the soln.

mixed in a colloid mill with the artificial resin soln. Molded articles may be produced by treating in a rubber-mixing mill 10 parts of rubber, 90 parts of phenol-aldehyde resin, 30 parts of β -dichlorohydrin and 20 parts of cyclohexanol, with or without fillers and S, evapng. the solvents, and pressing the mixt. in heated molds.

Rubber solutions. S. R. SHEPPARD. Brit. 192,163, Oct. 27, 1921. In rubber solns. to which a vulcanizing agent such as S_2Cl_2 is added, the vulcanizing agent is dissolved in a volatile non-inflammable medium. Two lbs. of rubber are dissolved in 6 gal. of CCl_4 or liquid $C_2H_2Cl_4$, and to this soln. is added 10 cc. of S_2Cl_2 dissolved in 1000 cc. of acetone and 1200 cc. of amyl acetate.

Attaching rubber to leather, etc. S. R. SHEPPARD. Brit. 192,164, Oct. 27, 1921. Unvulcanized rubber is attached to leather or other material by coating one or both of the surfaces to be joined with a rubber soln. contg. a vulcanizing agent dissolved in a volatile non-inflammable medium, and pressing the surfaces together. A suitable soln. is that described in 192,163 (preceding abstract).

Rubber-surfaced articles. W. HAINES. Brit. 193,137, Nov. 16, 1921. A rubber-contg. coating is applied to the surface of articles of wood, stone, cement, earthen ware, etc., by applying to the object a vulcanizing mixt. of rubber-contg. fibers, and subjecting the object to combined pressure and heat. The mixt. should contain not more, and preferably less than, 30% of rubber, and not less than 50% of fibers. Suitable fibrous materials are coconut fiber, sawdust, and asbestos. The invention is particularly applicable to the manuf. of rubber-surfaced wood paving blocks.

Vulcanizing latex. P. SCHUDROWITZ. Brit. 193,451, Sept. 24, 1921. A soln. or colloid suspension of vulcanized rubber in H_2O is obtained by submitting latex to vulcanization with S or the like under such conditions that coagulation is precluded. The latex must be rendered alk. to inhibit coagulation by the addn. of alkali as NH_3 , or a base as piperidine, or by the use of a vulcanizing agent such as an alk. polysulfide. Coagulation may also be prevented by diln. of the latex, or by the addn. of a colloid as casein, which also renders the final product less liable to be tacky. Typical example. 1.6 cc. of NH_3 is added to 100 cc. of latex contg. about 30% of rubber, and a cream consisting of 3 g. of S, 1 g. of ZnO , 1 cc. of piperidine in 35 cc. of H_2O is added. The whole is placed in a vulcanizer and vulcanized, $1/2$ hr. rise to 40 lb. and $1/2$ hr. at 40 lb., and the liquid is strained. Coagulation may be effected by the addn. of an acid, or by evapn. of the liquid, and the coagulation may be washed, milled, sheeted, etc. Articles may be coated with the liquid and dried, or sheets made by building up films. Fillers, dyes, etc., may be added at any stage. Cf. 18,497, 1910.

Puncture-sealing compositions. E. JACKSON. Brit. 192,213, Nov. 14, 1921. A compn. for injecting into the inner tubes of tires consists (a) $11\frac{1}{4}$ lbs. of shorts, $7\frac{1}{2}$ gal. of H_2O , $4\frac{1}{2}$ oz. of salicylic acid, 16 oz. of NH_3 (28% soln.); (b) $7\frac{1}{4}$ lbs. of powdered cork, 9 gal. of H_2O , 20 oz. of NH_3 ; (c) $18\frac{1}{2}$ lbs. of asbestos fiber, $10\frac{1}{4}$ gal. of hot H_2O , 50 gr. of methylene blue, 3 oz. of 40% $HCHO$. These mixts. are separately boiled, skimmed, mixed together, the following ingredients, viz., $6\frac{1}{2}$ oz. of tannin dissolved in 3 qt. of H_2O , $1\frac{1}{2}$ lbs. of creolin, $9\frac{1}{4}$ lbs. of Na_2SiO_3 soln., $1/2$ oz. of tannin, $1\frac{1}{2}$ oz. of carbolic acid in 3 gal. of H_2O , are added and the mixt. is boiled. While still hot, 18 lbs. of powdered asbestos, 50 gr. of methylene blue, 4 oz. of 40% $HCHO$, and 6 gal. of H_2O are added, the compd. is heated, 60 gr. of methylene blue, 3 oz. of $HCHO$ and 3 gal. of H_2O are added, the mixt. is again boiled and 3 lbs. of Na_2SiO_3 soln. is stirred in. After cooling for 24 hrs., sufficient H_2O and alc. are added to make 50 gal.

Vulcanizing rubber. S. M. CADWELL. U. S. 1,463,794, Aug. 7. Rubber is treated with S or other vulcanizing agent together with ZnO 10%, CS_2 5% and benzylamine 5% for vulcanization without necessity of the usual heating. Cf. C. A. 17, 2976.

Composition for preserving rubber articles. J. B. G. TABER. U. S. 1,464,143, Aug. 7. A mixt. of petrolatum 16 oz., lampblack 3 grains, cod-liver oil 80 grains, rubber gum 5 grains and C_6H_6 4 drams is used for coating rubber (e. g., tires or shoes).

Rubberized cord fabric. H. N. WAYNE. U. S. 1,464,632, Aug. 14. Cords are coated with hot plastic rubber and then assembled to form a web by cohesion.

Coating for rubber bales. E. HOPKINSON. Brit. 192,039, Oct. 24, 1922. See U. S. 1,442,218 (C. A. 17, 1351).

Extracting gutta-percha, etc. W. S. SMITH. Brit. 191,839, Oct. 21, 1921. Herbivorous animals are fed upon leaves of gutta-percha, etc., producing trees, their excrement is collected and washed to obtain the gum which passes through the animal unchanged.

